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The Conception of the Chemical Element as Enlarged by the Study of Radioactive Change.

A Lecture delivered before the Chemical Society on December 19th, 1918.

By FREDERICK SODDY.

THE Council of the Chemical Society have honoured me with the invitation to deliver one of three lectures bearing on the ultimate constitution of matter, and I accepted the invitation in my desire to show how greatly I appreciated it rather than with any prospect of being enabled, when the time came, to say anything on the subject which has not already been said before. The problem of the ultimate constitution of matter belongs to another world than that through which for the past four years we have been living, and although hostilities have at length ceased, and we may look forward to an opportunity of resuming in the future the thread of our philosophical investigations, philosophy herself is not so easily to be resumed. Novel in one sense as are the ideas introduced into the concepts of physics and chemistry by the study of radioactivity, four years' interruption has made them appear rather as a remote historical accomplishment than as a contemporaneous development. Although no longer new, however, the more as the subject matures does it become apparent that these advances are of fundamental and increasing importance to the chemist.

One would perhaps have expected that on the first and most

fundamental conclusion arrived at in the study of radioactive change that the change is of a transmutational character, involving the spontaneous disintegration of the radio-element into others, it would have been the chemists who would have been most deeply interested, and who would have weighed the evidence and pronounced a decision. Yet judgment on the view, which was put forward more than fifteen years ago, on evidence in my opinion even then deserving of serious consideration, although accepted and universally adopted by the workers in the subject and by physicists, has gone by default so far as the majority of chemists are concerned. From the first, much of the most important evidence has been of a singularly simple and convincing chemical character.

The Transmutational Character of Radioactive Change.

If a chemist were to purify an element, say lead from silver, and found, on re-examining the lead at a later date, that silver was still present, and, again and again repeating the process, found always that silver, initially absent, reappeared, would he not be forced to conclude that lead was changing into silver and that silver was being produced by lead? It is because of the absence of evidence of this kind that the doctrine of the unchangeability of the elements has grown up. One positive example of the kind in question and that doctrine would be at an end. The conclusion to which in 1902 Sir Ernest Rutherford and I were forced with regard to the element thorium was based on evidence of this direct and simple nature. By simple purification, by chemical and physical means, constituents responsible for the greater part of the radioactivity of thorium can be separated, and as often as they are separated they are regenerated at a perfectly definite and regular rate. One of these constituents, the emanation, is gaseous, and it can be separated from the thorium by no more elaborate means than by a puff of air. Certainly the actual quantity of thorium emanation is infinitesimal, but this did not hinder its complete chemical characterisation, for it was found to pass unabsorbed through every reagent tried, one or other of which would have absorbed every known gas with the exception of the gases of the argon family. The conclusion that the thorium emanation was a gas of the argon family produced by thorium, later extended to the similar gaseous products of radium and actinium, was a purely experimental conclusion reached before any theory whatever as to the nature of radioactivity had been advanced.

Another constituent responsible for part of the radioactivity we

called thorium-X. It is left in the filtrate when a solution of thorium is precipitated with ammonia, although not when the thorium is precipitated by other reagents, such as sodium carbonate or phosphate. After this removal, however, thorium-X re-forms in the thorium. Moreover, it is thorium-X, not thorium, that produces the emanation. The latter in turn produces the non-volatile active deposit, in which the successive products, called thorium-A, -B, -C, and -D, are now recognised. The false interpretation of a similar phenomenon in the case of radium, before the radium emanation had been recognised, led to the view that inactive matter could be rendered temporarily radioactive by "induction," through contact with or association with radioactive matter. In the case of thorium, the discovery of the chemical character of the thorium emanation rendered the nature of the phenomenon clear almost from the first.

This, taken in conjunction with the atomic character of radioactivity, recognised by Mme. Curie from the start, and with the fact that the law of radioactive change proved to be the same as the law of unimolecular reaction, made the conclusion that the radio-elements were undergoing a series of successive changes, in which new elements are produced, of chemical and physical character totally distinct from those of the parent element, the only one capable of explaining the facts.

Novel and unexpected as it was to find transmutation spontaneously in progress among the radio-elements, the phenomena this explanation explained were equally novel and transcended what to a generation ago would have appeared to be the limits of the physically possible.

It is to pay chemistry a poor compliment to represent this conclusion as in any way contrary to the established foundations of chemistry. If it had not been for the correct conception of the nature of chemical change, the clear distinction between atoms and molecules, and the conclusion that in all changes in matter hitherto studied the element and the atom of the element remain essentially unchanged, which we owe to the founders of chemistry, the character of radioactivity would not have been arrived at so quickly. On the other hand, if radioactivity had not been almost instantly recognised as a case of spontaneous transmutation, then, if you will, there would have been something radically wrong with chemistry and the training it affords in the elucidation of the metamorphoses of matter.

With regard, however, to the various claims that have been made since that transmutational changes can be artificially effected, by the aid of the electric discharge in gases or the rays from radium,

I have always regarded the evidence in this field as capable of simple alternative explanation. Different investigators have obtained entirely opposite results, and there is not that consensus of evidence one finds among those who have investigated radioactive change.

In another direction there has been a tendency to underrate the unique and unparalleled phenomenon of radioactive change, and to connect what is entirely and solely a development of the new experimental science of radioactivity, with the somewhat older isolation of the electron and the electronic hypotheses of the constitution of matter to which that discovery have given rise. For example, Sir J. J. Thomson in his Romanes Lecture, 1914, says: "Since the electron can be got from all the chemical elements we may conclude that electrons are a constituent of all the atoms. We have thus made the first step towards a knowledge of the structure of the atom and towards the goal towards which since the time of Prout many chemists have been striving, the proof that the atoms of the chemical elements are all built up of simpler atoms—primordial atoms, as they have been called." The removal of electrons from matter occurs in physical, chemical, and radioactive changes alike, exampled, respectively, by the electrification of a glass rod by friction, the ionisation of an electrolyte by solution, and by the β-ray change of radioactive substances. It is only in the latter case, however, that the electron can be regarded as a primordial constituent and the change as transmutational. Even to-day it is in radioactive phenomena, and in these alone, that the limits reached long ago in the chemical analysis of matter have been overstepped and the Rubicon, which a century ago Prout vaulted over so lightly in imagination, has actually been crossed by science.

First and Second Phases of Development.

Looking backward to the first recognition of the character of radioactive change in 1902, it is possible to distinguish broadly two phases. The first phase, concerned mainly with the disentanglement of the long and complicated series of successive changes, commencing with the two primary radio-elements uranium and thorium, and including ultimately all the known radio-elements, added little to the conceptions of chemistry beyond the disturbing fact that the radio-elements, although in every other respect analogous to the ordinary elements, are in process of continuous transmutation. But in the second and more recent phase of radioactive change, the study of the chemical character of the

successive products and the law connecting this with the type of ray expelled in the change, the discovery of elements with different radioactive but identical chemical character, the recognition of these as isotopes, or elements occupying the same place in the periodic table, and the interpretation of the significance of the periodic law, conceptions are arrived at which are not merely novel, but upsetting. In this phase, an aspect of the ultimate constitution of matter has been revealed that, although well within the scope of the conceptions of elements and atoms which we owe to the nineteenth century, nevertheless has totally escaped recognition. I am not much concerned with definitions, but I think the Chemical Society might safely offer a prize of a million pounds to any one of its members who will shortly and satisfactorily define the element and the atom for the benefit of and within the understanding of a first-year student of chemistry at the present time.

Chief Features of Radioactive Change.

The features that distinguish radioactive change from chemical change, and which have made it possible in a few short years to reduce to some degree of finality and completeness the intensely complicated series of successive changes suffered by the elements uranium and thorium in the course of their disintegration, are chiefly two. In the first place, the whole phenomena are inevitable, incapable of being changed or deviated from their allotted course by any means whatever, independent of temperature, concentration, or the accumulation of products of reaction, the presence of catalysts, irreversible and capable of being accurately and quantitatively followed without alteration or disturbance of the changing system. The mathematical theory, although for many successive changes it becomes cumbrous and unwieldy to a degree, involves only the solution of one differential equation by a device quite within the compass of anyone possessing a knowledge of the bare elements of the calculus to employ. The second feature is in the magnitude of the energy evolved, which, weight for weight of matter changing, surpasses that evolved in the most exothermic chemical changes known, from one hundred thousand to a million times. Manifested in the form of rays, by their fluorescent, photographic, or ionising power capable of being put into evidence in almost inconceivably minute amount, changes are capable of being followed, and by the electroscope accurately measured, which would conceivably require to continue for millions of years before they could be experimentally detected by chemical or even by spectroscopic methods. The disintegration of the single

atom is ascertainable, for example, in the spinthariscope of Sir William Crookes, where each of the scintillations separately visible is due to the impact of a single α-particle on the zinc sulphide screen. On the same principle, methods have been developed and are in regular use for counting the number of atoms disintegrating per minute, whereas to the spectroscope at least $3 \cdot 10^{13}$ atoms as a minimum must be present, 25,000 times as many atoms as there are human beings alive in the world, before any element can be so detected. By the most curious compensation, almost of the nature of a providential dispensation which some may have found difficult to believe, the quantity of matter of itself is not of importance in investigating radioactive change. The methods depend on the rate of emission of energy, and this is proportional to the quantity of the changing element multiplied by its rate of change. In the disintegration series, the various members accumulate in quantities inversely proportional to the rates of change, and so it comes about that all changes within the series are equally within the scope of the method whether, as in the case of the parent elements, they involve periods surpassing the most liberal estimates of the duration of geological time or, as in the case of the C' members, are estimated to run their course in a time so short that light itself can travel but a very few millimetres, before the next change overtakes the changing atom.

The condition of radioactive equilibrium in which the quantities of the successive products assume the above stationary ratio is of course entirely different from chemical equilibrium, and is the condition in which for each member of the series except the first as much is produced as changes further in the unit of time.

The foregoing applies so long as the changes continue. When they are finished and it is a question of ascertaining the ultimate products, the task may be likened to that of searching for a meteor which a moment before lit up the heavens and now has vanished into the night.

The Ultimate Products.

It is a matter for surprise that in all radioactive changes so far studied there appear to be only two ultimate products, helium and lead, the former constituting the α-particles and the latter being produced both by uranium and thorium, withal, as we now know, not the same lead in the two cases. There are sufficient experimental reasons for doubting whether the disintegration of an atom into more nearly equal parts would be within range of detection by any of the known methods. A heavy atom like oxygen, for example, if expelled as a radiant particle, might not attain

sufficient velocity to ionise gases, or, even if it did, the range over which the ionisation would extend, as we know from the ionisation produced by the recoil atoms, would be extremely small. It must be a matter for comment, however, that hydrogen never appears in these changes, as, if it were produced, it would almost certainly be as easy to ascertain as helium. It has always seemed to me a possibility that some genetic connexion may exist, after all, between thorium and uranium, although I have never been able to frame even a possible mode of so connecting these two elements. With a difference of atomic weight of six units, it is impossible to pass from one to the other by addition or expulsion of helium atoms alone.

Both with regard to helium and lead, the composition of radio-active minerals gave the first clue to the identity of the ultimate products. After the discovery of radioactivity and the elucidation of its nature, the fact that helium was found only in minerals containing uranium and thorium assumed a totally new interpretation, borne out by the spectroscopic proof of the production of helium from radium by Sir William Ramsay and myself, and later from actinium, polonium, and even from uranium and thorium, all at the rates to be expected from radioactive data. The identification of the α-particle with helium, after the weight of the α-particle had been shown by new physical methods to be four times that of the hydrogen atom, was accomplished by enclosing the radium emanation in a glass tube thin-walled enough to allow the α-particle to go through, but perfectly impervious to the passage of gas. In these circumstances, helium in spectroscopically detectable quantity was proved by Rutherford to make its appearance outside the tube.

Such confirmations by the spectroscope, welcome and gratifying as they are, are nevertheless in a sense subsidiary to the main problem, namely, the task of unravelling the complicated series of changes into its individual steps, and the characterisation by their radioactivity of the several intermediate members of the series, such as by the determination of their periods and the physical constants of the radiation α-, β-, or γ-, to which they give rise. The determination of their chemical character, although equally important, was only later fully accomplished.

The Radiations.

In the successive radioactive changes, α- or β-particles are expelled, one α-particle per atom disintegrating for each change, although for the β-particles our knowledge is less exact. In some

cases, certainly, although these are exceptional, β-particles seem to be expelled along with α-particles. The α-particle is an atom of helium charged with two atomic charges of positive electricity, or, as we should now say, is the helium nucleus, deprived of the two electrons which are combined with it in the helium atom. The β-particle is the negative electron, and when expelled with sufficiently high velocity is accompanied with γ-rays. The latter are X-rays of exceedingly short wave-length, varying from 1·3 to 0·1 Ångström units.* A connexion exists between the speed of the change and the speed of the particles expelled, and the more rapid the change the faster in general and the more penetrating are the attendant α- or β-particles. In the case of the α-particle, an empirical logarithmic relation, known as the Geiger-Nuttall relation, enables us to calculate approximately the period of the changing element from the velocity or range of the α-particle, and vice versa, and by this means periods too long or too short to be directly measurable have been estimated. In the case of the β-rays, no definite quantitative law has yet been made out, but it is clear that a similar relationship must exist. One of the important corollaries is that changes much slower than the slowest known, namely, those of uranium and thorium, would probably not be detectable, as, even were α- or β-particles expelled, they would be of too low velocity probably to ionise gases or show fluorescent or photographic actions. Indeed, for mesothorium-*I* and actinium this appears to be the case. No detectable radiation is expelled, although the products conform to what would occur in β-ray changes. The period of both substances is long, and it is probable that the β-particle is expelled, but is undetectable by ionisation methods. For the slowest β-ray change, that of radium-*D*, with a period of twenty-four years, the β-radiation is of such low velocity as to be only capable of detection by special care, and is far less penetrating than average α-rays. These facts serve to show that changes may be going on in the non-radioactive elements which at present are beyond experimental means of detection.

Period of Average Life.

The law of radioactive change, which is the same for all cases, is that of unimolecular reaction, the rate of change, or quantity changing in unit of time, being a fraction, designated by λ and

* The shortest wave-length so far resolved by the crystal reflection method is 0·072 Å. in the spectrum of the γ-rays of radium-*C*. Ishino and Rutherford have recently concluded, however, that the main γ-radiation of radium-*C* must have a wave-length lying between 0·02 and 0·007 Å. (*Phil. Mag.*, 1917, [vi], **33**, 129; **34**, 153.)

known as the radioactive constant, of the amount present. The value of λ, although vastly different for different radio-elements, is an absolute constant, so far as is known, for any one element, independent of every consideration whatever. The period of average life is the reciprocal of this constant, but the actual life of any one atom may assume any value. This is an experimental fact very difficult to account for. For example, it is quite easy to compare the value of λ for a collection of atoms (1) only just produced and not in existence a short interval before, and (2) that have remained undistinguished from an originally very much greater number, and each of which has been in existence many times the period of average life. In both cases the value of λ is the same. This fact excludes from consideration as a conceivable cause of disintegration any gradual progressive alteration in the atom during its period of existence, as, for example, was at one time suggested, a gradual radiation of internal energy by the electrons in their orbits within the atom. So far, we must admit, the cause of atomic disintegration remains unknown, although Lindemann (*Phil. Mag.*, 1915, [vi], **30**, 560) has attempted, with some success, to frame a theory to account for it.

Branch Series.

The development of the various radioactive sequences revealed that sometimes the series branches, and that in the change of one radio-element sometimes two products result, in general, in different amounts. Thus the uranium series at one point branches into the radium and actinium series, in proportion 92 to 8 out of 100 atoms disintegrating. Again, in the case of radium-C and thorium-C a similar branching occurs, and here in one branch an α-ray change is followed by a β-ray change, and in the other branch the sequence is reversed. These cases are sufficiently explained if it be supposed that two simple radioactive changes are in progress in the same substance simultaneously, and that each obeys the law of simple change as though the other did not occur. The distribution of the original substance into the two products is then proportional to the relative rates of the two changes. If λ_1 and λ_2 are the radioactive constants of the two changes, the proportion between the two products is as λ_1 to λ_2, and the constant of the double change as a whole, $\lambda_1 + \lambda_2$. For thorium-C, the ratio is as 65 to 35, but for radium-C 99·97 to 0·03. The first is relatively easy, but the second extremely difficult to follow experimentally. It is, for example, impossible to follow further what occurs to the minor branch owing to the minuteness of the quantity

of material, and although this has to be represented as not further changing, we have only negative evidence to go on. This branching is very important as showing how from one element two products or more in very different quantity may result, and may be the explanation of the excessive rarity of certain of the elements in nature.

History of the Analysis of Matter.

The second, and in many respects even more revolutionary phase in the development of the study of radioactive change arose out of the chemical characterisation of the successive products, but some historical comment on the various influences which have gone to shape the current conception of the chemical element may be of interest before dealing with this development.

The analysis of matter into different chemical elements was at first concerned with known materials obtainable in abundance. The question, then, was not as to the existence or otherwise of certain elements, but whether certain thoroughly well-known substances were elements or compounds. Boyle's original celebrated definition was a purely practical one. That was to be regarded as elementary which could not by any means be separated into different substances. Almost at once, however, there crept into the interpretation of this conception two fallacies, or two aspects of the same fallacy, implicit in all the later characterisations of the elements, right up to the present time, namely, first that chemical analysis was necessarily the most fundamental and searching kind of material analysis, known or to be discovered, and, secondly, that chemical compounds were necessarily more difficult to resolve than simple mixtures. *Any* means soon came to mean any chemical means, and the element, in consequence, the chemical element. So was taken the first step which ultimately was to make the term *chemical element,* as it is at present understood, denote a definite but highly complex chemical conception, incapable of being defined or even understood without long years of training in the science, and totally different in every single respect from what a plain man or a beginner in the subject might reasonably suppose the term element ought to connote. The elementary and even the homogeneous character has departed from the conception of the chemical element, but the conception remains, and, whatever we choose to call it, will remain. The criterion of the chemical element soon came to be, in fact, the possession of a unique chemical character, distinguishing it and sufficing for its separation from all other elements. To this Dalton added a new criterion, the magnitude of the weight of the atom of the element, and each

element unique in chemical character (as it happened) proved also to possess a unique atomic weight.

The discovery of the periodic law introduced the idea of families of chemically analogous elements, the members of which recurred after regular intervals when the elements were arranged in order of atomic weight. With the exception of hydrogen, every element became one of a group all totally distinct, but with obvious similarities. Boyle's practical definition of the element as that which could not be further resolved, more and more, as the century advanced, fell into desuetude. It became replaced by a theoretical conception, to which subsequently I propose to apply the term "heterotope," meaning the occupant of a separate place in the periodic table of elements. With this place came to be associated the unique chemical character, unique atomic weight, and later unique spectrum. On the claims of a substance to the title of element, as in settling disputes as to what multiple of the equivalent was to be adopted as the atomic weight, the periodic law became the court of appeal. Did a claimant to the title of element fit into a vacant place in the family of related elements? If it did, not only was there no doubt as to its atomic weight, but it certainly could scarcely be an ordinary compound or mixture. Whatever the elements were, it was clear that they were all of a class, the limits of chemical analysis, and, if complex, then all probably of the same kind of complexity.

Incidentally, also, the periodic law showed that although there was a connexion between atomic weight and chemical character, there were exceptions, like tellurium and iodine, where the atomic weights appeared to have been reversed. This made it perfectly plain that it was merely a chance that no two elements happened to possess the same atomic weight. Dalton, as we shall come to describe, discovered in the atomic weight not merely a new atomic property, but a new class of atomic property which, until the present century, remained the only one of the kind known, and is concerned with a different region of the atom from that to which physical and chemical character, position in the periodic table, spectrum, and other identifying characteristics are to be referred.

The discovery of spectrum analysis led to the recognition of many new elements, cæsium and rubidium, thallium, indium, helium, and gallium all being so recognised before anything at all was known as to their other properties. In each case unique spectrum was later found to correspond with unique chemical character—except for the argon gases, all characterised by absence of chemical character—and unique atomic weight.

Again, the first fruits of the discovery of radioactivity were the

recognition of the new elements polonium, radium, and actinium
by their unique radioactive character in the first place. Then, in
the case of radium, its claim to the title of element was confirmed,
first by its exhibiting a unique spectrum, then by its possession of
unique chemical character and atomic weight and by its occupy-
ing a vacant place in the periodic table. The emanations, next,
as occupying a place in the family of argon gases, were easily
characterised, and for the radium emanation unique spectrum
was proved. Its origin from radium by loss of one α-particle gives
the atomic weight as 222, which agrees with determinations of its
density and rate of diffusion. The chemical characters of
polonium and of actinium are different from those of the elements
they most closely resemble. Polonium, or radium-F, by its close
chemical analogy to both bismuth and tellurium, was characterised
as an element of the sulphur family occupying the vacant place
contiguous to bismuth. Actinium, by its resemblance in chemical
character to the rare earths, and especially to lanthanum, although
capable of being concentrated fractionally from that element, was
reasonably supposed to occupy the vacant place in Group III,
between radium and thorium. As will later appear evident, both
these elements in due course may be expected to show unique
spectra.

Further progress in the elucidation of the chemical character
of successive products then underwent an abrupt and, at first,
very puzzling change of direction. As member after member in
the series was distinguished and characterised by its unique radio-
active character, by its disintegration in definite and characteristic
ways at definite and characteristic rates, no further *chemically*
new elements were discovered. *Unique radioactive character does
not always, as it did with radium, imply unique chemical and
spectroscopic character*. The new members resembled known
elements in chemical character so closely that they could not be
separated from them by chemical analysis, although sharply
differentiated from them by the radioactive properties. Radio-
lead or radium-D cannot be separated from the lead which, being
a product of uranium, accompanies it always in uranium minerals.
Ionium, the direct parent of radium, cannot be separated from
thorium; but the most instructive case, historically, which shows
well how the new method of radioactive analysis serves to dis-
tinguish different elements, where chemical analysis fails, was the
case of radiothorium.

Chemically Non-separable Elements.

Ramsay and Hahn, in the course of working up a large quantity of thorianite for radium, observed in fractionating the radium 'from the barium in the usual way that the activity of the material concentrated at both ends of the fractionation.   The activity accumulating in the more soluble fractions was due to a new product, which they termed radiothorium.   It produces thorium-X, the thorium emanation, etc., in successive changes.   Naturally enough, they thought they had separated radiothorium by chemical processes from thorium, but they had not, for that, as we know, is quite impossible.   Then Hahn found along with the other end fraction, containing the radium, a further new product, mesothorium, which is intermediate between thorium and radiothorium. The radiothorium they had separated from thorianite was not that present in the mineral when they started, but that which had re-formed from the mesothorium after it had been separated from the thorium in the mineral.   Could any more elegant extension, not merely of knowledge, but of the means of obtaining knowledge, be imagined?   Two different elements, thorium and radiothorium, which on account of their chemical resemblance could not be individually recognised, and in the original interpretation of the thorium disintegration series were taken as one, became individually knowable, because the latter is the product of the former through the intermediary of a third member, mesothorium, possessing chemical properties totally unlike either.   Radioactive change thus became the means of a new analysis of matter, for which there is no counterpart outside the radio-elements.

In turn, mesothorium suffered analysis into two successive products, mesothorium-1 and -2, the first distinguished by long period of life and a rayless disintegration into the second, which has a short life and gives powerful β- and γ-radiation in its change into radiothorium.

I then found that mesothorium-1 was chemically non-separable from radium, a discovery also made by Marckwald at the same time, and in 1911 I pointed out that in an α-ray change, such as ionium into radium, radium into emanation, thorium into mesothorium-1, and other cases, the expulsion of the α-particle causes the radio-element to shift its place in the periodic table by two places in the direction of diminishing mass and diminishing valency, whereas in successive changes in which α-particles are not expelled, it frequently reverts to its former position, as, for example, radiothorium from mesothorium and lead from radio-lead.

To those actually engaged in the task of trying to separate the

successive products of radioactive change by chemical analysis, it soon became clear that the chemical resemblances disclosed between certain of the members was such as to amount to chemical identity. The most obstinate cases of similarity previously known, among the rare earths, for example, cannot be compared with them. In all cases, radioactive methods afford the most delicate means for detecting the least alteration in the concentration of the constituents, and the most prolonged and careful attempts fail to produce a detectable separation.

At my request, Fleck undertook in my laboratory a systematic chemical examination of all the members of the series still imperfectly characterised, from the point of view of first finding which known element they most resembled and then finding whether or not they could be separated from that element. His researches were the means of finally unmasking the extreme simplicity and profound theoretical significance of the process of radioactive change. All the members of the series so far chemically uncharacterised he found to be chemically non-separable from one or other of the known elements, mesothorium-2 from actinium, radium-A from polonium, the three B-members and radium-D from lead, the three C-members and radium-E from bismuth, actinium-D and thorium-D from thallium.

Radioactive Change and the Periodic Law.

In February, 1913, K. Fajans in Germany, from electrochemical evidence, and in this country A. S. Russell and I independently, from Fleck's work, pointed out the complete generalisation which connects chemical character and radioactive change. In addition to the shift of two places in the periodic table caused by the expulsion of the α-particle, it was now clear that the expulsion of the β-particle caused a shift of one place in the opposite direction. Since the α-particle carries two atomic charges of positive electricity and the β-particle one atomic charge of negative electricity, the successive places in the periodic table must thus correspond with unit difference of charge in the atomic structure, a conclusion reached later for the whole periodic table, as far as aluminium, as the result of Moseley's investigations on the frequency of Barkla's characteristic X-radiations of the elements.

The non-separable elements, with identical chemical character, on this scheme were found all to occupy the same place in the periodic table, and on this account I named them isotopes. Conversely, the different elements recognised by chemical analysis should be termed "heterotopes," that is, substances occupying

separate places in the periodic table, but themselves mixtures, actually proved or potential, of different isotopes, not necessarily homogeneous as regards atomic weight and radioactive character, but homogeneous as regards chemical and spectroscopic character, and also physical character, so far as that is not directly dependent on atomic mass.

Spectra of Isotopes.

As regards the spectrum, the first indication that chemically non-separable elements probably possessed identical spectra arose out of the failure of Russell and Rossi and of Exner and Haschek in 1912 to detect any lines other than those of thorium in the spectrum of ionium–thorium preparations that might reasonably be supposed to contain an appreciable, if not considerable, percentage of ionium.   The work of Hönigschmid on the atomic weight of ionium–thorium preparations has fully confirmed this view.   The isotopes of lead of different atomic weight separated from uranium and thorium minerals have been found to possess identical spectra.   For this element, lead, Rutherford and Andrade have shown that the secondary γ-radiation excited by the impact of β-rays on a block of ordinary lead gave by crystal reflection two lines identical in wave-length with the two strongest lines in the γ-ray spectrum of radium-B, an isotope of lead, as Fleck showed, of atomic weight 214.   This is of importance as indicating that X-rays and γ-rays, although no doubt originating in a deeper region of the atom than the ordinary light spectrum, do not originate in the deepest region of all to which the weight of an atom and its radioactive properties are to be referred.

Description of the Figure.

The generalisation, brought up to date, is set forth in the accompanying figure, which is to be read at an angle of 45°, making the lines of atomic weight horizontal and the division between the successive places in the periodic table vertical.   Starting from uranium and thorium, the series run in an alternating course across the table and extend over the last twelve places as far as the element thallium.   At this point, it is interesting to note that the expulsion of an α- instead of a β-particle would have resulted in the production of an isotope of gold, and so literally have realised the goal of the alchemist.   As it happens, a β-particle is expelled and lead results, so far as the changes have yet been traced, in all cases as the final product.

· It has been necessary, in order to separate the series from one

another, to displace the actinium series to the right and the radium
series to the left of the centre of the places, but this displacement
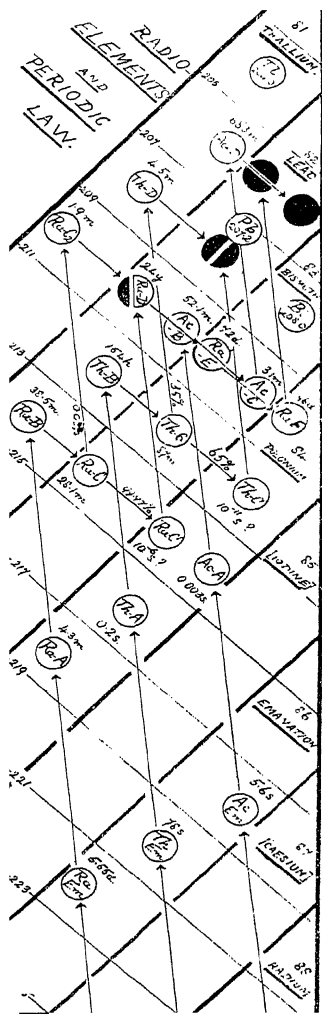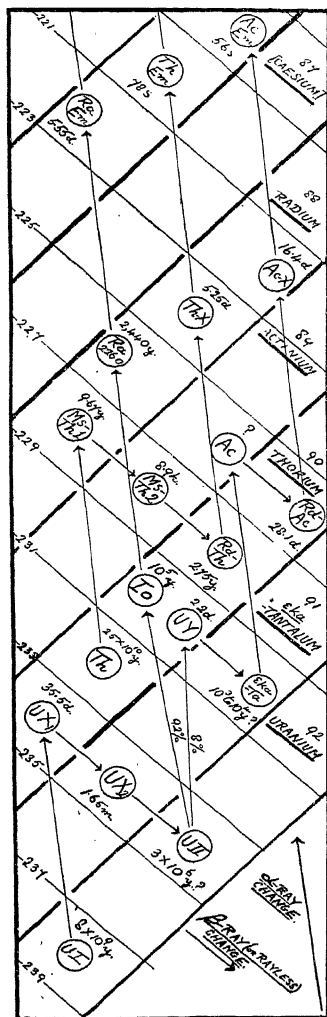
within the single place is not intended to express any physical
significance; but for the fact that many members would be super-

imposed, they would all be represented in the centre of the places. The periods of average life, which are always 1·443 times the periods of half-change, are shown for each member above or below its symbol, a ? indicating that the period is estimated indirectly from the Geiger-Nuttall relation.

The figures at the head of each place represent the atomic numbers or number of the place in the periodic table, starting with hydrogen as unity, helium as 2, lithium as 3, and so on. Moseley found that the square-root of the frequency of the characteristic X-radiation of an element was, for the K-series of radiations, proportional to integers less by one than the atomic numbers. Strictly speaking, there is no means of determining the absolute value of the atomic number, but the starting point having been fixed for any one element, the others can then be found in terms of it.   Moseley assumed the atomic number of aluminium as 13, as it is the thirteenth known element in the list starting with hydrogen as unity.   It is unlikely that any new elements will be discovered between hydrogen and aluminium,* although if they were it would be necessary to alter the whole of the subsequent atomic numbers to correspond.   For X-radiations of the other series, the square-roots of the frequencies are not proportional to integers even, although the differences are nearly integral for successive elements in the periodic table.   The actual numbers in the figure, 92 for uranium, for example, are derived from the assumption that the atomic number of aluminium is 13, but it is well to remember that, although relatively to one another based on experimental evidence, the absolute value is to some extent arbitrary.

The Chemical Character of the Radio-elements.

The simple connexion between the sequence of radioactive changes and the chemical character of the products has effected an enormous simplification, not only in the theory, but also in the practice of radio-chemistry.   The series extends over twelve places, two, namely, those in the families of the halogens and the alkali metals, being entirely skipped.   In the ten occupied places are forty-three distinct types of matter, but only ten *chemical* elements.   Seven of these ten, thallium, lead, bismuth, emanation, radium, thorium, and uranium, can now in every respect be considered, both chemically and spectroscopically, thoroughly well

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* The position of the stellar elements of Prof. Nicholson it is unnecessary to consider here, as the Chemical Society is shortly to be given a first-hand account of this fascinating question.

known. These seven places accommodate all but nine of the known radio-elements, and these nine, the isotopes of polonium, actinium, and ekatantalum, respectively, are the only members the chemistry and physics of which cannot be referred to well-known elements obtainable in sufficient quantity for ordinary chemical and spectroscopic examination.

Of these three, polonium, although the element of which at present the chemistry is best known, is likely to remain the most difficult to bring into line with the others, for, although a vast amount of exact information has been obtained as to its reactions, it would seem to remain hopeless ever to obtain it in anything but infinitesimal amount owing to its relatively very short period.

The chemistry of actinium has been enormously simplified by the discovery that mesothorium-2 is isotopic with it, for the latter may be used as an indicator to show in what way the actinium distributes itself after any chemical treatment. Owing to its relatively small quantity as a branch product and to the fact that, itself, it gives no rays, the characteristic radioactivity of its products only making their appearance slowly after it has been separated, actinium has always been a difficult element to extract from the mineral and very easy to lose in chemical operations. There is now, however, another reason which will assist in the study of this element.

The Origin of Actinium. Ekatantalum.

The generalisation has now led to the elucidation of its origin and the discovery of its direct parent. From its constant association with uranium minerals, and the relative activity therein of its products in comparison with the activity of those of radium, it was considered to be a branch product of the uranium series, only 8 per cent. of the atoms of uranium disintegrating passing through the actinium series and 92 per cent. through the radium series. Its definite location in the periodic table, by virtue of its isotopy with mesothorium-2, made it clear that its parent must either be in the radium or the ekatantalum place, the former if it is produced in a β-ray change and the latter if it is produced in an α-ray change.

The ekatantalum place was vacant when the generalisation was first made, but it was necessary to suppose that uranium-X, like mesothorium, comprised two successive products, uranium-X_1 and uranium-X_2, both giving β-rays, and the latter occupying the vacant place in question. This prediction was confirmed within a few weeks of its being made by the discovery by Fajans and

Göhring of uranium-X_2, or brevium, a new member responsible for the more penetrating β-radiation given by uranium-X, and having a period of only 1·65 minutes. The possibility that actinium was produced in a β-ray change from an isotope of radium was experimentally disproved, and there remained only the second alternative, which was rendered the more probable by the existence of a member, uranium-Y, discovered by Antonoff, isotopic with uranium-X_1, and simultaneously produced with it from uranium in relative quantity such as is to be expected, if it were the first member of the actinium series. Uranium-Y, like uranium-X_1, gives soft β-rays, and hence its unknown product must be the isotope of uranium-X_2, and might also well prove to be the unknown direct parent of actinium in an α-ray change of long period.

During the year the missing element has been found in two independent investigations (Soddy and Cranston, *Proc. Roy. Soc.*, 1918, [*A*], **94**, 384; O. Hahn and L. Meitner, *Physikal. Zeitsch.*, 1918, **19**, 208). The problem as it presented itself to us was so to treat a uranium mineral as to separate an element, if present, which possessed the chemical character of the known but hopelessly short-lived uranium-X_2, using the latter as an indicator in trying possible methods beforehand. The method adopted, distillation at an incipient red heat in a current of carbon tetrachloride vapour and air, was found to be very effective in volatilising uranium-X_2 from uranium-X_1, and when applied to pitchblende it was found to give a product in which none of the known pre-emanation members of the disintegration series were present. Thus was obtained a preparation from which actinium was at first absent, but which, with the lapse of time, continuously generated actinium, as characterised beyond the possibility of doubt by means of its active deposit.

It should be mentioned that the exact point at which the uranium series branches has not yet been definitely ascertained, as there is a choice of alternatives, at present experimentally indistinguishable. Uranium-Y may be either the product of uranium-*I* or of uranium-*II*, and the latter alternative, which is that shown in the figure, is taken for the present as likely to be on the whole the more probable. The point can only be settled by the determination of the atomic weight of ekatantalum or actinium.

Independently, Hahn and Meitner obtained the parent of actinium from the insoluble siliceous residues left after the treatment of pitchblende with nitric acid by adding tantalum, and then separating it and purifying it by chemical treatment. They showed that it gave α-rays of range 3·314 cm. of air at *N.T.P.*, and, from this range, estimate its period to be from 10^3 to $2 \cdot 10^4$

years.   There should therefore be sufficient of the element in
uranium minerals to enable the spectrum, atomic weight, and
chemical character of the pure substance to be determined in the
same way as for radium.   Its separation on a large scale will
enable actinium itself to be grown in a pure state, analogously to
the preparation of radiothorium from mesothorium, and so should
allow the spectrum at least of actinium to be found.

With regard to the period of actinium, there is at present a real
conflict of evidence, and so it is impossible to say whether our
knowledge of actinium is ever likely to become as complete as that
of radium, or to remain, like that of polonium, confined to what
can be learned from infinitesimal quantities.   Cranston and I, on
certain assumptions, concluded from indirect evidence that the
period of actinium was 5000 years, but Hahn and Meitner, on the
other hand, state that they have obtained evidence confirming
Mme. Curie's provisional estimate of the period as about thirty
years, from the direct observation of the decay of the radiations
of a sealed actinium preparation.

Atomic Weight of Isotopes.

It is clear that the periodic law connects, not primarily chemical
character and atomic weight, but chemical character and atomic
charge or atomic number, which alters its value by integers, not
continuously, producing the step-by-step changes in chemical
character which is at the basis of the analysis of matter into the
chemical elements, or heterotopes.   This atomic number is, how-
ever, the algebraic sum of positive and negative charges, so that
the loss of the α-particle with its two positive charges and of two
negative electrons as β-particles leaves its value unchanged and
produces an isotope of the element having an atomic weight four
units less than the original.   Unique chemical character and
unique spectrum reaction is no proof of homogeneity, and so we
arrive at the conclusion that the chemical elements, so far con-
sidered homogeneous, may be mixtures of isotopes, possessing
different atomic structure and stability, revealed when they
undergo radioactive change, and in some cases also different atomic
weight.   This, although within the scope of the Daltonian analysis
of matter to detect, nevertheless, until radioactive investigations
revealed this possibility, remained overlooked.   In two cases, that
of the isotopes of lead on the one hand, and of ionium and thorium
on the other, this difference of atomic weight in elements spectro-
scopically and chemically identical has now been established by
direct determinations.

The figure shows that, so far as these changes have been followed, they all terminate in the place occupied by lead, and, if this is the real, as distinguished from the apparent end in all cases, all the ultimate products are isotopes of lead with atomic weight between 210 and 206. The product of radium-C_2, in the branch claiming only 0·03 per cent. of the whole ultimate product of radium, with atomic weight 210, may be left out of account as being negligible, and also the product of the actinium branch for which the atomic weight is still uncertain; but the main products, namely, that of uranium with atomic weight 206, and both the thorium products in the two branches, with atomic weight 208, are different in different directions from that of common lead with atomic weight 207·2.

The conclusion that the ultimate product of thorium, as well as of uranium, was lead, was quite new and opposed to the opinion of those who had made a special study of the Pb/U and Pb/Th ratios of radioactive minerals of various geological periods. I found, however, that the atomic weight of the lead separated from Ceylon thorite was 207·7, and Hönigschmid confirmed this with a specimen of my material and obtained the figure 207·77. Just recently, from a specimen of lead separated from a Norwegian thorite by Fajans and his co-workers, he has found the value 207·90 (*Zeitsch. Elektrochem.*, 1918, **24**, 163). Whereas the same investigator, and also T. W. Richards and others, have found values for the atomic weight of lead separated from uranium minerals all lower than that of common lead, and in two cases from carefully selected minerals between 206·0 and 206·1. I found my thorite lead was denser than common lead in the same proportion as its atomic weight was greater, and the densities of the various specimens of uranium lead have been found by Richards to be less than that of common lead, the atomic volume for all varieties being constant. The spectra of these various isotopes have been repeatedly examined, but hitherto no differences whatever have been established.*

The atomic weight of a mixture of ionium and thorium was found by Hönigschmid to be 231·51 as compared with 232·12 for thorium, the spectra being identical and impurities absent in both specimens. The calculated value for the atomic weight of ionium is 230, and the evidence, so far as it yet goes, is in accord with

* Haskins and Aronberg (*Proc. Nat. Acad. Sci.*, 1917, 3, 710), for ordinary lead and uranio-lead of atomic weight 206·34, examining the strongest line, 4058, in the sixth order of spectrum obtained by a 10-inch grating, observed a constant difference of 0·0043 Å., but are themselves disposed to await further results before drawing any conclusions. ·

the view that, in the mixture examined, about 30 per cent. was ionium and 70 per cent. thorium. By a simple comparison of the emanating power of the mixture with that of the pure thorium preparation under similar conditions, the proportion of ionium to thorium could be readily determined directly, since ionium does not give an emanation, and this unknown eliminated, but this has still to be done.

The Different Varieties of Isotopes and Heterotopes.

When isotopes, such as those just considered, possess different atomic weights, it is to be expected, although this has not yet been practically accomplished, that a separation by physical means, such as prolonged fractional diffusion, ought to be possible. Chlorine and other elements, the atomic weights of which depart largely from an integral value, seem to deserve a further physical analysis by this method. Sir J. J. Thomson's positive-ray method of gas analysis ought to be able to detect such isotopes of different atomic weight without separation, and at one time it seemed that neon had been so resolved, but this has not yet been confirmed.[*] It would be interesting also if the rotation of the salts of some optically active acid with different varieties of lead, separated from uranium and from thorium minerals, were examined. A difference is to be expected, although it is likely to be small, and possibly may be too minute to be detectable. Recent experiments at Harvard have shown that the refractive index of a crystal of lead nitrate is independent of the atomic weight of the contained lead, but the solubility, as is to be expected, is different, the molar solubility of different varieties being the same.

Isotopes need not, however, have different atomic weights. One of the clearest cases is in the two end-products of thorium, but, if the scheme is correct as regards the branching point of the actinium series, ionium and uranium-Y, actinium-A and radium-C', actinium-C and radium-E, actinium-B and radium-D, and the actinium and uranium isotopes of lead, are other cases. These result by branchings of the series, and, since in the respective branches the amount of energy evolved in the successive changes is different, the internal energy of the various pairs must be different, although for them atomic weight as well as spectroscopic and chemical character are all identical. I recently suggested in the case of the two end-products of thorium that possibly only one of these survives in geological time, namely, that produced in the

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[*] Mr. Ashton tells me this work is still being actively prosecuted at the Cavendish Laboratory.

smaller quantity, and that the other continues to break up in changes as yet undetected (Royal Institution Lecture, May 18th, 1917; *Nature*, 1917, **99**, 414 and 433).   This would account for the relative poverty of thorium minerals in lead, which was the original basis for the conclusion that lead was not the ultimate product of thorium.   The point still remains experimentally untested.   Isobaric isotopes of the character in question can only at present be distinguished if they are unstable and break up further, but they must be taken into account in any theoretical conception we form of the ultimate structure of matter.   The accomplishment of artificial transmutation would reveal them if they existed, and the discovery of any new property, like radioactivity, concerned with the nucleus of the atom rather than its external shell, might also be the means of revealing differences of this character.

On the other hand, the production of isobaric heterotopes is the ordinary consequence of β-ray changes, single or successive.   Such heterotopes, possessing different chemical and spectroscopic character but the same atomic weight, have been recently termed *isobares* by A. W. Stewart (*Phil. Mag.*, 1918, [vi], **36**, 326), who, following Fleck's work on the chemical resemblance, not amounting to non-separability, between quadrivalent uranium and thorium, has drawn a parallel between them and elements existing in more than one state of valency, as, for example, ferrous and ferric iron.

The extent to which the study of radioactive change has enlarged the conception of the chemical element may be summarised by the statement that now we have to take into account in our analysis of matter, not only the heterobaric heterotopes before recognised, but also heterobaric and isobaric isotopes and isobaric heterotopes or isobares.

The Nuclear Atom.

I have attempted to present the most important facts of radioactive change without introducing any theory or hypothesis at all as to the structure of the atom.   I think it important to keep the two matters distinct.   Our knowledge of electricity, which in its modern phase may be considered to start from the relatively recent discovery of the electron, is still far too imperfect to enable any complete theory of atomic structure to be formulated.   My task would be incomplete, however, if I did not refer briefly to the nuclear atom of Sir Ernest Rutherford, which may be regarded as the logical descendant of the earlier electronic atom of Sir J. J. Thomson.   The weakness of the latter was that it took account essentially only of the negative electrons, and its attempt to ascribe

the whole mass of the atom to these nearly massless particles involved the supposition that a single atom may contain hundreds of thousands of electrons. The actual number is now known to be rather less, as an average, than half the numerical value of the atomic weight. Although unsatisfactory in accounting for the mass of the atom on an electronic basis, it was much more in line with present views in accounting for chemical character and the arrangement of elements in the periodic table. The root idea that the successive elements in the table are distinguished by the increment of one electron in the outermost electronic ring, followed, as period succeeds period, by the completion of this ring and the formation of a new external one, so that members of the same chemical family have similar external ring systems, is still the most probable view yet advanced. In conjunction with the conception of the nucleus and the gradual unravelling of the various series of characteristic X-radiations, both experimentally and by mathematical analysis, it bids fair soon to give a definite concrete picture of the structure of all the different elements (compare L. Vegard, *Phil. Mag.*, 1918, [vi], **35**, 293).

As regards the deepest region of atomic structure, wherein radioactive phenomena originate, the nuclear atom is the only one proposed that has any direct experimental foundation. It is based on the deflections suffered by the α-particle in its passage through the atoms of matter, on the one hand, as Bragg showed many years ago, on the exceedingly slight deviation of the overwhelming majority of the α-particles, and, on the other, on the subsequently discovered large deviations suffered by a minute proportion. The nuclear atom is a miniature solar system, like most model atoms, the negative electrons occupying the atomic volume by their orbits around a relatively excessively minute central sun or nucleus, wherein the atomic mass is concentrated, and consisting of an integral number of atomic positive charges equal to the atomic number of the element, and the number of electrons in the outer shell. An α-particle is the nucleus of the helium atom, and, unless it passes very near the nucleus of the atom through which it penetrates, its path is practically undeflected. The few that chance to pass close to the exceedingly small but massive central nucleus are swung out of their path like a comet at perihelion, save that the forces at work are regarded as repulsive rather than attractive.

It appears from radioactive change that atomic disintegration occurs always in the central nucleus, both α- and β-particles originating therein. The atomic number of the element is its nett nuclear charge, the difference between the positive and

negative charges entering into its constitution. Of all properties, mass and radioactivity alone depend on the nucleus; the physical and chemical character and the spectrum of an element originate in the outer shell. The character of the outer shell is fixed by the nett charge, not at all by the mass or internal constitution of the nucleus, and the integral variation of this charge from 1 to 92 gives the successive places of the periodic table. Expulsion of two β- and one α-particle in any order gives an isotope of the original element with atomic weight four units less. Isobaric isotopes resulting in branch changes differ only in the internal structure and stability of the nucleus. The atomic mass is the only nuclear property known before the discovery of radioactivity, and, except as regards this, the whole of physics and chemistry up to the close of the nineteenth century had not penetrated beyond the outer electronic shell of the atom. Even now, mass and radio-activity remain the sole nuclear properties known.

Conclusion.

Nemesis, swift and complete, has indeed overtaken the most conservative conception in the most conservative of sciences. The first phase robbed the chemical element of its time-honoured title to be considered the ultimate unchanging constituent of matter; but since its changes were spontaneous and beyond the power of science to imitate or influence to the slightest degree, the original conception of Boyle, the practical definition of the element as the limit to which the analysis of matter had been pushed, was left essentially almost unchanged.

The century that began with Dalton and ended with the discoveries of Becquerel and the Curies took the existing practical conception of the chemical element and theorised it almost out of recognition. The element was first atomised, and then the atom was made the central conception of the theory of the ultimate constitution of matter, on which modern chemistry has been reared, and from which its marvellous achievements, both practical and theoretical, have mainly sprung. The atom and the element became synonyms, related as the singular to the plural, and implicit throughout this century was the assumption that all the atoms of any one element are identical with one another in every respect. The only exception is in Sir William Crookes's conception of " meta-elements " as applied to the rare earths. Here the idea was rather that of a gradual and continuous difference among the different atoms of the same element, the properties of the latter

being the mean of those of its individual atoms. Modern developments have tended definitely away from rather than towards this view.

The second phase in the development of radioactive change has now negatived each and every one of the conceptions of last century that associated the chemical element with the atom. The atoms of the same chemical element are only chemically alike. Unique chemical and spectroscopic character is the criterion, not of a single kind of atom, but rather of a single type of external atomic shell. Different chemical elements may have the same atomic mass, the same chemical element may have different atomic masses, and, most upsetting of all, the atoms of the same element may be of the same mass and yet be an unresolvable mixture of fundamentally distinct things. Present-day identity may conceal differences for the future of paramount importance when transmutation is practically realised. Then it may be found that the same element, homogeneous in every other respect, may change in definite proportion into two elements as different as lead and gold. The goal that inspires the search for the homogeneous constituents of matter is now known to be, like infinity, approachable rather than attainable. The word homogeneity can in future only be applied, qualified by reference to the experimental methods available for testing it.

All this, of course, does not in the least affect or minimise the practical importance of the conception of the chemical elements as understood before these discoveries. Every chemist knows the conception has had and will continue to have a real significance as representing the limit of the spectroscopic and chemical analysis of matter which remains, although it now is known to convey something very different from the original and natural conception of the chemical elements as the l m n's of the material alphabet.

I.—*The Dilution Limits of Inflammability of Gaseous Mixtures. Part III. The Lower Limits of some Mixed Inflammable Gases with Air. Part IV. The Upper Limits of some Gases, Singly and Mixed, in Air.*

By Hubert Frank Coward, Charles William Carpenter, and William Payman.

Part III.

In Part I of this series of papers (Coward and Brinsley, T., 1914, **105**, 1859), the wide variation in the values assigned by different observers to the limits of inflammability of hydrogen and other gases in air was shown to be due to the very different criteria of inflammability used. The meaning of the term "inflammability" was therefore discussed, and it was concluded that inflammability could and should be regarded as a characteristic property of a gas mixture, apart from the precise means used for ignition and from the form of the vessel that might happen to be chosen for experiment. It was argued that a gaseous mixture should be termed inflammable *per se* at a stated temperature and pressure if, and only if, it were capable of indefinite self-propagation of flame, while the unburnt portion of the mixture was maintained at the stated temperature and pressure.*

In Part II (T., 1914, **105**, 1865), the lower limits of inflammability of hydrogen, methane, and carbon monoxide individually in air were examined experimentally by means of apparatus specially designed to enable the progress of flame to be observed in much wider and longer vessels than had been hitherto employed.†

The present paper records the results of experiments carried out to determine the lower limits in air of various mixtures of hydrogen, methane, and carbon monoxide taken two at a time or

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* This definition has been discussed by Burgess and Wheeler (T., 1914, **105**, 2591). Several other papers on the subject of "dilution limits of inflammability" have appeared since Coward and Brinsley's paper was published, but as they have not been concerned with the question of indefinite propagation of flame, but merely with the inflammation of very limited amounts of gaseous mixtures, they have no direct bearing on the present inquiry.

† Burrell and Oberfell (U.S.A. Bureau of Mines, *Technical Paper*, No. 119, 1915) have adopted a eudiometer of the same size as that used by Coward and Brinsley.

all three together, and, finally, of the complex mixture, a "town's gas."

A simple formula, of purely additive character, has been put forward by Le Chatelier to connect the lower limits of single gases with the lower limits of mixtures of them. This formula, originally limited to binary mixtures, is generalised thus:

$$\frac{n_1}{N_1} + \frac{n_2}{N_2} \qquad \frac{n_3}{N_3} \qquad\qquad 1.$$

where N_1, N_2, N_3 . . . are the lower limits, in percentages of the whole air mixture, for each combustible gas separately, n_1, n_2, n_3 . . . are the proportions, in percentages of the whole air mixture, of each combustible gas at the dilution limit. The percentage of total combustible gas present in the limit mixture is thus $L = n_1 + n_2 + n_3 + \ldots$

This formula enables the lower limit, L, of a combustible mixture to be calculated from the dilution limits of its several constituents. If the proportions of each of the combustible constituents are p_1, p_2, p_3 . . ., so that $p_1 + p_2 + p_3 + \ldots = 100$, a simple transformation gives its dilution limit in air as

$$L = n_1 + n_2 + n_3 + \frac{100}{\dfrac{p_1}{N_1} \quad \dfrac{p_2}{N_2} + \dfrac{p_3}{N_3}}$$

The physical meaning of the formula may be best appreciated by the consideration of a particular case. A mixture of air, carbon monoxide, and hydrogen which contains one-quarter of the amount of carbon monoxide necessary to form a lower limit mixture, together with three-quarters of the amount of hydrogen necessary, will be a lower limit mixture. In other words, the lower limits of inflammability form a series of inflammability equivalents for the individual gases of a mixture.

It may also be deduced from the formula that lower limit air mixtures, if mixed in any proportions, give rise to mixtures which are also at their lower limits.

Experimental support for the formula rests on observations by Le Chatelier (*Ann. des Mines*, 1891, [viii], **19**, 388) with three mixtures of methane and coal gas, by Le Chatelier and Boudouard (*Compt. rend.*, 1898, **126**, 1344) with three mixtures of hydrogen and carbon monoxide and with one mixture of acetylene and carbon monoxide, and by Eitner (Habilitationsschrift, München, 1902) with hydrogen and carbon monoxide in equal volumes and with coal gas. The difference between the calculated and the observed dilution limits rarely reached one twenty-fifth part of

the combustible mixture. None of these experiments, however, was carried out in apparatus large enough to indicate whether the mixtures used were capable of continued propagation of flame. Thus, Le Chatelier and Boudouard used for the lower limit of hydrogen in air the figure 10 per cent., whereas the recent experiments have shown that mixtures containing upwards of 4·1 per cent. of hydrogen are capable of propagating flame apparently indefinitely in an upward direction. Le Chatelier had, in fact, found that the 10 per cent. hydrogen mixture was the weakest which would propagate flame downwards through a somewhat narrow tube. It is only necessary to ignite from below to produce a self-propagating flame in mixtures considerably weaker in hydrogen.

The experiments now to be described were therefore carried out in the eudiometer previously described (Coward and Brinsley, *loc. cit.*), 1·8 metres (6 feet) in length and 30 cm. (1 foot) square in section, with a capacity of 170 litres.

In each case, the mixtures under experiment were saturated with moisture at 18—19°, and were maintained at approximately atmospheric pressure during inflammation. The source of ignition was a spark gap of variable length between small platinum spheres. A 6-inch Apps coil with two, four, or six storage cells was used to produce single sparks. The various gases were prepared in a state of purity, and each mixture with air was made to the desired composition, which was checked by the analysis of samples taken just before firing.

EXPERIMENTAL.

The lower limits of a number of mixtures of hydrogen, carbon monoxide, and methane, taken two or three together, and also of a "town's gas," are recorded in table I (p. 30), together with the lower limits calculated by means of the Le Chatelier formula from the limits of the individual gases.

Several of the experimental results differ from those calculated by amounts exceeding the errors of observation and experiment; nevertheless, the formula gives a useful approximation over the whole range of mixtures examined, and may be applied, therefore, to water gas and to coal gas, as well as to town's gas.

The most striking anomaly was shown by the mixture containing 10 per cent. of hydrogen and 90 per cent. of carbon monoxide, where the large difference was in the opposite direction to that usually noted. This anomaly was more pronounced in experiments with the same mixture in a narrower tube (5 cm. diameter).

TABLE I.

Composition of gas (before admixture with air).			Lower limit of inflammability in air.		
Hydrogen.	Carbon monoxide.	Methane.	Observed. Per cent.	Calculated. Per cent.	Difference. Per cent.
100	—	—	4·1	—	—
75	25	—	4·7	4·9	— 0·2
50	50	—	6·05	6·2	— 0·15
25	75	—	8·2	8·3	— 0·1
10	90	—	10·8	10·4	+ 0·4
	100	—	12·5	—	—
—	90	10	11·0	11·1	— 0·1
—	75	25	9·5	9·6	— 0·1
—	50	50	7·7	7·7	0·0
—	40	60	7·2	7·1	+ 0·1
—	25	75	6·4	6·5	— 0·1
—	—	100	5·6*	—	—
25	—	75	4·7	5·0	— 0·3
50	—	50	4·6	4·7	— 0·1
75	—	25	4·1	4·4	— 0·3
90	—	10	4·1	4·2	— 0·1
100	—	—	4·1	—	—
33·3	33·3	33·3	5·7	6·0	— 0·3
55	15	30	4·7	5·0	— 0·3
	" Town's gas " †		5·35	5·36‡	0·0

* This figure is chosen, rather than the lower value given by Coward and Brinsley (*loc. cit.*, p. 1885) for the reason stated on page 1877 of that paper : " . . . the flames of mixtures containing 5·3 to 5·6 per cent. of methane are very sensitive to extinction by shock . . . a 5·6 per cent. mixture will invariably propagate flame when the shocks are no greater than those occasioned by the somewhat violent bubbling of gas through water . . . (but) when the circumstances are such that a tranquil passage is assured, 5·3 per cent. is the lower limit of inflammability of methane in air." In none of the present experiments with methane mixtures did we observe the curious tranquil passage of flame noted with the 5·3 per cent. methane mixture, so that 5·6 per cent. seems the correct figure to employ for calculations in connexion with these experiements.

† Composition of the " town's gas " : C_6H_6, etc., vapours=0·8. CO_2=2·6. O_2=0·5. C_2H_4 etc.=2·8. CO=14·1. H_2=46·6. CH_4=19·4. C_2H_6=4·0. N_2=9·2 per cent. The benzene, etc., vapours were estimated by the determination of their partial pressures, by Burrell and Robertson's method (*J. Ind. Eng. Chem.*, 1915, 7, 669).

‡ For calculating this figure, the following lower limits of the individual gases were used : Hydrogen, carbon monoxide, and methane, as in table I, ethylene 3·4 per cent. (Eitner), ethane 3·1 per cent. (Burgess and Wheeler), benzene 1·4 per cent. (Kubierschky). The last three values represent results obtained in small vessels, but may probably be safely used in view of the comparatively small amounts of the three gases present in the " town's gas."

The non-inflammable constituents of the town's gas amounted to 12·3

A brief reference to the general character of the flames is necessary. Inflammable mixtures rich in hydrogen, including the town's gas, gave thin vortex rings of flame, increasing in diameter as they rose through the first 30 or 40 cm., and then breaking into luminous segments, which subdivided into balls of flame. The latter rose, increasing in number, to the top of the vessel. The flames in mixtures somewhat below the lower limit were extinguished at some stage of their journey. The flames of these mixtures showed, in fact, similar behaviour to those described by Coward and Brinsley for pure hydrogen, but the luminosity was much enhanced. Inflammable mixtures containing no hydrogen gave thick rings which, as they progressed, developed into flames of strongly convex front spreading from side to side of the box; similar mixtures just below the limit of inflammability gave rings of flame breaking into striæ, which were extinguished in the next 50 or 100 cm. of their journey. The appearance of all the flames of mixtures is apparently compounded additively of those of the individual components.

There was no difficulty in deciding upon the figure for the limit within about 0·1 per cent.

Conclusions (Part III.).

The lower limits of inflammability, in air, of mixtures of hydrogen, carbon monoxide, and methane, taken two at a time or all together, and also the lower limits of water gas, coal gas, and town's gas, may be calculated with approximate accuracy from the lower limits of the individual gases by means of Le Chatelier's formula.

PART IV.

The Upper Limits of some Gases, Singly and Mixed, in Air.

The upper limits of inflammability of hydrogen, methane, and carbon monoxide severally in air have been investigated by a number of observers; their results are quoted in T., 1914, **105**, 1859. The hydrogen figures show the greatest range of variation, namely, from about 55 to 80 per cent. of hydrogen. The methane figures mostly lie between 12 and 17 per cent. of methane, and

per cent., which on the lower limit mixture represents only 0·66 per cent. of the whole. In view of the known slight influence on the lower limit of methane of the substitution of small amounts of carbon dioxide or nitrogen for equal amounts of air, it is safe to assume for the purposes of the calculation that the non-inflammable constituents of coal gas (and likewise of water gas) can be treated as air.

the carbon monoxide figures are in the neighbourhood of 75 per cent. of carbon monoxide.

The Upper Limit of Hydrogen.—Some preliminary experiments were conducted with the object of discovering whether the flames in mixtures just below the upper limit resembled the flames in mixtures just above the lower limit. If so, the apparent discrepancies between the results of earlier workers might be explained on the same lines as the discrepancies noted in lower limit figures. It was soon evident, however, that comparatively weak or short electric sparks, which were quite strong enough to ignite lower limit mixtures, were unable to inflame upper limit mixtures. Stronger sparks in the latter mixtures started flames which travelled throughout the whole mixture. This promised a clue to the main cause of discrepancy of the results of others, and by the use of igniting sparks of such variable strength as might well have ·been employed in ordinary laboratory practice, a range of results was obtained nearly as wide as those of the previous uncorrelated list. The experiments were carried out in a half-litre globe with a spark of variable length in the centre. A 6-inch Apps induction coil was used with a constant break, and the current in the primary was varied by using a battery of 2 to 12 volts. We have to acknowledge our indebtedness to Mr. F. Brinsley for conducting this series of experiments, the results of which are recorded in table II.

TABLE II.

Percentage of Hydrogen in Apparent Upper Limit Air Mixture.

	Voltage of accumulators.			
Spark gap.	2	4	8	12
1 mm.	57·5		67·0	—
2	—		70·2	—
4	—		71·2	—
8	70·2	70·7	71·2	72·2
16	—		72·5	—
20	—		—	74·5
32	—		73·5	—
45	—		—	75·5
56	—		73·5	—

These figures suggest an upper limit of hydrogen–air mixtures in the neighbourhood of 75·5 per cent. of hydrogen, but the volume of gas used was much too small to indicate whether the flames observed were capable of indefinite self-propagation. Furthermore, the gases were confined, and so were not maintained under constant pressure during inflammation.

FIG. 1.   FIG. 2.

Hydrogen.   *Methane.*

FIG. 3.   FIG. 4
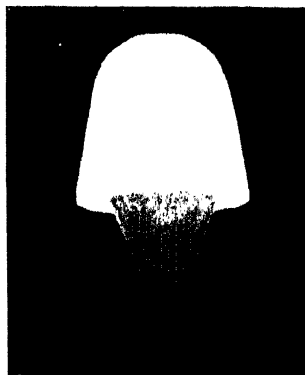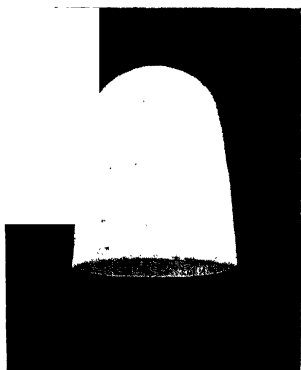
Carbon monoxide.   *Methane and carbon monoxide mixture.*

Upper limit flames, in tube of 5 cm. diameter.

A series of experiments was therefore carried out in a 15-litre bell-jar, just dipping under the surface of water, with a spark gap near the bottom of the mixture. With a suitable single spark, ignition was obtained with mixtures containing 73·1, 73·8, and 74·0 per cent. of hydrogen, but failed with 74·4 and 75·0 per cent. of hydrogen. The flames travelled rapidly throughout the whole mixture. The limit indicated was thus approximately 74·2 per cent. of hydrogen.

The next step in determining the true limit for continued propagation of flame was the use of long vessels. A tube 1·5 metres long and 5 cm. wide was used. Flame travelled rapidly through this tube with mixtures containing 71·2 and 71·4 per cent. of hydrogen. The appearance of this flame is indicated in Fig. 1. Mixtures containing 71·6 and 73·0 per cent. could not be ignited, or, if ignited, the flame was extinguished before it had travelled more than a few cm. from the spark.

In order to fix the upper limit precisely, it would be necessary to use vessels of dimensions comparable with those of the box previously described. This would involve the construction of a much stronger vessel than the one available, but at the time this was contemplated, the experiments had to be abandoned, and opportunities for continuing them will not be available in the near future.

It is, however, certain that the upper limit of hydrogen is somewhat higher than 71·5 per cent.; it is probably near to 74·2 per cent.

The Upper Limit of Methane.—In the 15-litre bell-jar, mixtures containing 15·1 and 15·3 per cent. of methane propagated flame, of a reddish-brown colour edged with blue, upwards throughout the mixture. A 15·5 per cent. mixture could not be ignited, but when a rapid succession of sparks was passed, a blue flame-cap was observed above them.

In the 1·5-metre tube, mixtures containing 14·4, 14·7, 15·0, and 15·1 per cent. of methane propagated flame throughout the tube; with a 15·2 per cent. mixture, a flame was initiated, but was extinguished after passing some cm. up the tube. In each case, the flame seemed to consist of two distinct portions, the uppermost blue with a convex front, followed by a reddish-brown conical tail, which suggested a secondary reaction of combustion (see Fig. 2). The limit for indefinite propagation is therefore more than 15·1 per cent., and probably approaches 15·4.

This conclusion is supported by the experiments of Burrell and Oberfell (*loc. cit.*), who used for upper limit experiments on methane an iron pipe 30 cm. (12 inches) in diameter, 2·1 metres

(7 feet) high, with a series of glass windows. Their experiments showed the upper limit to lie between 15·0 and 15·4 per cent. for upward propagation of flame.

The Upper Limit of Carbon Monoxide.—In the 15-litre bell-jar, flames travelling rapidly upwards through the whole of the mixture were obtained when 73·7 and 74·0 per cent. of carbon monoxide was present. Flames were initiated in 74·5 and 75·0 per cent. mixtures, but were extinguished after travelling a short distance. A 75·2 per cent. mixture gave only a blue halo round the spark.

In the 1 5-metre tube, a flame travelled up through a 72·9 per cent. mixture, but no more than a tongue of flame was obtained with a 73·1 per cent. mixture. The walls of the tube evidently exerted a notable cooling influence. The self-propagating flame had a strong convex front, was blue with a bright whitish-blue edging, but had no "tail," as was the case with methane flames (see Fig. 3).

The limit for indefinite propagation is therefore more than 73·0 per·cent., and probably approaches 74·2 per cent.

Applicability of the Mixture Law to Upper Limits of Inflammability.

The additive character of the lower limits of inflammability was expressed by Le Chatelier in a formula quoted above (p. 28). The validity of a similar formula for the upper limits of mixed combustible gases in air has been obscured by experiments with hydrogen–air mixtures in which the sparks were insufficiently strong, and therefore the figures obtained represented, not the limiting composition for the propagation of flame, but the limiting composition for the initiation of flame by the sparks in use. It is shown below that the following formula holds approximately for the upper limits of mixtures of hydrogen, methane, and carbon monoxide, two or three at a time·

$$\frac{n_1}{N_1} \quad \frac{n_2}{N_2} + \qquad\qquad = 1$$

where n_1, n_2 . . . represent the proportions, in percentages of the whole air mixture, of each combustible gas, at the upper limit, N_1, N_2 . . . represent the upper limits, in percentages of the whole air mixture, of each combustible gas separately.

For reasons stated above, the experimental apparatus available did not combine the desirable width with the desirable length, and the choice lay between a bell-jar and a longer but narrower

glass tube (1·5 metres long, 5 cm. in diameter). The latter was chosen because it enabled a flame to be observed travelling far enough from the original source of ignition; the disadvantage of narrowness was not great, for the limits observed in the tube were lower than those indicated by the wider bell-jar by a not very considerable amount. (For hydrogen, 2·7 on 74·2 per cent.; for methane, 0·25 on 15·4 per cent.; for carbon monoxide, 1·2 on 74·2 per cent.)

The limits observed in the tube are recorded in table III.

TABLE III.

| | Percentage composition of gas (before admixture with air) | | | Upper limit of inflammability, in air. | | |
	H_2.	CH_4.	CO.	Observed.	Calcu-lated.	Differ-ence.
Single gases ...	100	—	—	71·5	—	—
	—	100	—	15·1	—	—
	—	—	100	73·0	—	—
Binary mixtures.	48·5	51·5	—	22·6	24·4	−1·8
	50	—	50	71·8	72·5	−0·7
	—	50	50	22·8	25·0	−2·2
Ternary mixture	33·3	33·3	33·3	29·9₍	31·9₍	−2·0
Coal gas	See footnote.*			30·9	28·8†	+2·1

* Composition of the coal gas. C_6H_6, etc. $= 1·2$; $CO_2 = 0·1$; $O_2 = 0·1$ $C_2H_4 = 2·9$; CO $= 7·3$; $H_2 = 50·6$; $CH_4 = 29·7$; $C_2H_6 = 3·2$; $N_2 = 4·9$ per cent.
† For the calculations, the upper limits of hydrogen, methane, and carbon monoxide given in the table were used, together with the values $C_6H_6 = 4·7$ (Roszkowski) ; $C_2H_4 = 22·0$; $C_2H_6 = 10·7$ (Burgess and Wheeler, ignition centrally in large globe. Private communication).

Analyses of the residual gases showed that mixtures just below the upper limit propagated flames which consumed the whole of the oxygen, and therefore passed through the whole of the mixture. This behaviour is in sharp contrast with that of lower limit mixtures, in which self-propagating flames may leave unconsumed a considerable fraction of the mixture.

Figs. 1, 2, and 3 show that the upper limit methane flames are characterised, in contradistinction from the hydrogen and carbon monoxide flames, by the possession of flame tails. Mixtures containing methane with carbon monoxide or hydrogen and air also exhibit the remarkable tail, which suggests a secondary reaction (see Fig. 4). Evidence as to the nature of this reaction should be readily obtained by an examination of the interconal gases,

but the opportunity of attempting this experiment has not pre-sented itself.

<div align="center">Conclusions (Part IV.).</div>

The upper limits of inflammability in air, saturated with water at 18—19°, of hydrogen, methane, and carbon monoxide are in the neighbourhood of 74·2, 15·4, and 74·2 per cent. respectively.

The upper limits in air of mixtures of these gases, taken two or three at a time, and also the upper limit of coal gas, may be calculated with approximate accuracy by means of a simple formula of an additive character.

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II.—*The Propagation of Flame through Tubes of Small Diameter.   Part II.*

By WILLIAM PAYMAN and RICHARD VERNON WHEELER.

IT is a common practice at collieries to test the safety of the miners' flame lamps, before they are taken underground, by intro-ducing them into an inflammable mixture of coal-gas and air.

It is known that the speed of propagation of flame in mixtures of coal-gas and air can be considerably faster than in any mixture of methane and air. Since any inflammable mixture into which a miner's lamp may accidentally be introduced in the practice of coal mining is produced exclusively by fire-damp, and since it is a rare occurrence for fire-damp to contain even traces of any in-flammable gas other than methane, the use of mixtures of coal-gas and air for testing the security of a lamp for use underground is justifiable only on the grounds of providing an adequate "margin of safety." The use of coal-gas becomes unjustifiable if the margin of safety thereby provided is excessive; for every additional pro-tective device embodied in the construction of a miner's flame safety-lamp militates against the proper ventilation of the lamp, and therefore diminishes its light-giving power.

It is thus of importance to be able to make an exact comparison between the speeds of propagation of flame in mixtures of coal-gas and air and fire-damp, or methane, and air under similar conditions of experiment. Furthermore, since the rapid speed of flame in coal-gas–air mixtures is, presumably, due mainly to the hydrogen contained therein, and since different qualities of coal-gas contain

different proportions of hydrogen, it is necessary to obtain information regarding the effect of varying the proportions of the constituent gases in coal-gas on the speed of propagation of flame in its mixtures with air.

Following the same methods of experiment as with mixtures of fire-damp and air (T., 1918, **113**, 656), the speeds of the uniform movement of flame in mixtures with air of coal-gas, hydrogen, and a 1:1 methane–hydrogen mixture have been determined in glass tubes of different small diameters for comparison with the results obtained with fire-damp–air mixtures in similar tubes. Comparative experiments have also been made on the projection of flame through brass tubes of small diameter.

For the experiments with mixtures of coal-gas and air, a supply of gas from the main was stored over alkaline water in a metal gas-holder of 70 litres capacity; and the mixtures with air were made in smaller glass gas-holders from this supply. In this manner, variations in the composition of the coal-gas, such as would have occurred had the gas for each mixture been drawn direct from the main, were avoided.

Rather more gas was required to complete the series of experiments than was anticipated, so that it was found necessary to recharge the storage-holder before all the information desired was obtained.

From one point of view this was unfortunate, for the second charge of gas differed slightly in composition from the first, and mixtures with air of the one could not be directly compared with mixtures with air of the other. From another point of view, however, the enforced use of samples of coal-gas of different compositions was not to be regretted, for there were found to be marked differences in the speeds of propagation of flame in mixtures with air of the two qualities of gas. This observation led at once to the determination of the speeds of flame in mixtures with air of what may be termed a "synthetic coal-gas," containing equal parts by volume of methane and hydrogen. The results obtained, taken in conjunction with the known values for methane–air and hydrogen–air mixtures under the same conditions of experiment, are of considerable theoretical interest, whilst they should also prove of practical value.

According to Le Chatelier ("Le Carbone," p. 266. Paris, 1908), if several combustible gases are mixed together with air, the following relation exists at the lower limit of inflammability of the mixture, between the limits of inflammability N and N' of each of two gases and their proportions n and n' in the limit mixture:

$$n/N + n'/N' = 1.$$

Coward, Carpenter, and Payman have shown (this vol., p. 28) that this formula can be applied with considerable accuracy to a number of mixtures of gases, and that it holds also at the upper limit of inflammability.

The formula implies that if a limit mixture with air of one inflammable gas is mixed in any proportion with a limit mixture with air of another inflammable gas, a limit mixture results. Another way of stating the relation, in an expanded form, is as follows :

$$L = 100 / \left(\frac{a}{L_a} + \frac{b}{L_b} + \right. \tag{i}$$

By means of this equation, the limiting percentage, L, for a mixture of gases can be found directly from the known limits of the individuals; a, b, . . . being the percentages of the individuals in the mixed inflammable gases, and L_a, L_b, . . . their respective limits.

The subject of the calculation of the limits of inflammability of mixed combustible gases is introduced here because a similar formula holds with remarkable accuracy (considering the nature of the phenomena under investigation) for calculating the speeds of flame in mixtures with air of a composite combustible gas like coal-gas, the speeds in mixtures of the individual gases with air being known.   The formula is:

$$S \qquad \frac{a + b +}{a/S_a + b/S_b +} \tag{ii}$$

in which S is the speed required; a, b, . . . the percentages of the different combustible gases in the mixed gas (coal-gas, for example); and S_a, S_b, . . . the corresponding speeds of flames in mixtures of the individuals with air.

This formula necessarily finds its readiest application in the calculation of the speeds in distinctive mixtures, namely: (1) the limit mixtures, upper and lower, in which the speed of flame is slowest; and (2) the mixtures in which the speeds of flame are fastest.   For such mixtures, the agreement between calculated and observed speeds is close.

In the table that follows are given: (1) the limits of inflammability, with horizontal propagation of flame in a glass tube 9 mm. in diameter, for hydrogen, methane, and a mixture of equal parts of hydrogen and methane; and (2) the speeds of the uniform movement of flame, in a horizontal glass tube 9 mm. in diameter, with the lower- and upper-limit mixtures and in the mixtures with the fastest speeds of flame, for hydrogen, methane, and the 1 : 1 hydrogen–methane mixture.   The calculated limits and speeds for

the hydrogen–methane mixture, as determined by equations (i) and (ii), respectively, are also given.

	Limits. Lower.	Per cent. Upper.	Speeds of uniform movement of flame. Cm. per second.		
			Lower-limit mixture.	Mixture with fastest speed.	Upper-limit mixture.
Hydrogen	6·7	65·7	8·3	430	(50)
Methane	7·8	11·6	32·6	49	35·6
Hydrogen– (Obs.) methane	7·2	19·6	13·7	96	17·1
mixture (Calc.)	7·2	19·7	13·2	90	(42)

The value obtained for the speed of propagation of flame in the upper-limit mixture of hydrogen and air is not the true value, which should approximate to that of the speed in the lower-limit mixture. The probable reason for the discrepancy is explained later. Omitting this value, and the calculated value for the speed of flame in the upper-limit mixture of hydrogen–methane–air based on it, it will be seen that there is a close correspondence between the calculated and the observed values for the limits and speeds.

With coal-gas, the gases that preponderate are hydrogen and methane, which in the two samples, A and B, used for these experiments totalled 83·5 and 85 per cent. respectively. Ignoring the other gases, calculation according to equation (ii) gives 106 and 96 cm. per second, respectively, as the maximum speed obtainable during the uniform movement of flame in a tube 9 mm. in diameter in mixtures of each sample of coal-gas with air. The speeds as determined by chronographic means were 106·2 and 94 cm. per second.

The proportion of mixed gases to be added to air to give mixtures with the fastest speed of the uniform movement of flame can also be calculated, knowing the corresponding values for each individual gas. The fastest speed with mixtures of methane and air is obtained over the range 9·5—10·0 per cent. of methane; with mixtures of hydrogen and air, the range is 38—45 per cent. of hydrogen. Using the same type of formula as for calculating the limit mixtures, the "fastest speed mixtures" of air with mixed combustible gases are found to be as follows:

Combustible gases.	Mixtures with air in which the speed of the uniform movement of flame is fastest. Per cent. of combustible gas.	
	Calculated.	Observed.
Hydrogen–methane,		
(1 : 1)	15·2—16·3	15·0—16·0
Coal-gas A	17·5—18·8	18·0—19·0
Coal-gas B	16·3—17·5	16·5—17·5

If equation (ii) is expressed in the form

$$a/S_a + b/S_b + \quad . \quad . \quad = \quad \frac{a + b + \ \cdot \ \cdot \ \cdot \ \cdot}{S_{a+b+} \ \cdot \ \cdot \ \cdot \ \cdot}$$

it is at once apparent that the inverse of the speed of flame in mixtures of a composite gas with air is a simple additive property of the inverse of the speed of flame in each constituent gas with air. In other words, the time taken for flame to spread through a given volume of a mixture of combustible gases with air, under the conditions of combustion during the uniform movement, is the mean of the times taken for flame to spread through the same

Fig. 1.

Combustible gas in air. Per cent.
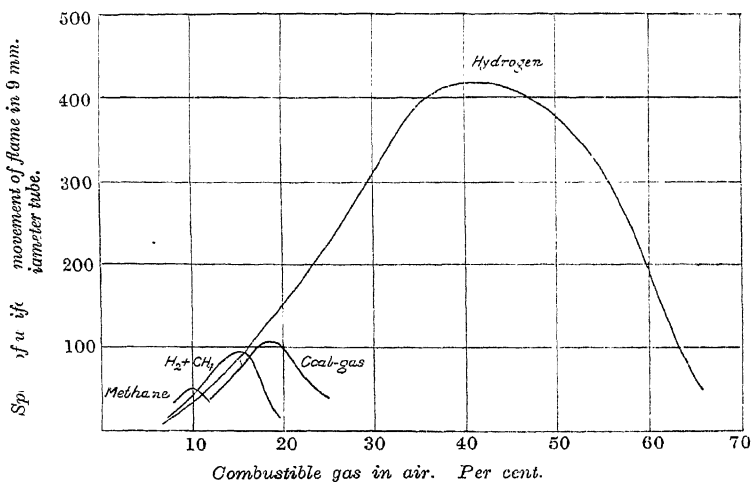
volume of mixtures of each constituent gas with air if present alone.

No doubt this relation, which has been shown to hold true for the fastest and the slowest speeds of the uniform movement of flame, is true also, as suggested by the generalisation just stated, for intermediate speeds. So that, given the necessary data respecting the individual combustible gases, the behaviour of flame in any mixture of several with air can be deduced. The exposition of the validity or otherwise of this assumption, when three or more combustible gases in varying proportions are used, will form the subject of a subsequent communication.

In Fig. 1 are shown, plotted to the same scale, the speed–per-

centage curves, for the uniform movement of flame in a horizontal glass tube 9 mm. in diameter, for hydrogen and methane, for a 1:1 mixture of hydrogen and methane, and for coal-gas (sample *A*).

The curve for hydrogen is constructed from Haward and Otagawa's determinations (T., 1916, **109**, 85), with additional figures obtained near and at the limiting percentages. In this connexion, it should be noted that Haward and Otagawa, though they made no attempt to determine accurately the limits of inflammability for horizontal propagation of flame, considered that in a tube 9 mm. in diameter flame would not travel horizontally in mixtures containing less than 11·8 or more than 63·5 per cent. of hydrogen. Actually, the limits under the conditions thus specified are 6·7 (lower) and 65·7 (upper) per cent. It was found that when igniting mixtures near the limits of inflammability, great care had to be exercised to avoid disturbance at the mouth of the tube, and for that reason a lighted taper, such as was employed by Haward and Otagawa, which answered admirably over the range of mixtures studied by them, was unsuitable.*

* The details of the determinations made to locate the limits of inflammability of hydrogen–air mixtures in a horizontal tube 9 mm. in diameter are as follow : the tube was 1·5 metres long and the mixtures were ignited by a secondary discharge across a 5 mm. gap 4 cm. from the open end of the tube.

Lower limit. Hydrogen, per cent.	Result.
9·4	Flame travelled throughout.
7·5	,, ,, ,,
7·1	,, ,, ,,
6·8	,, ,, ,,
6·6	Incomplete propagation of flame.

These results place the lower limit at 6·7 per cent. hydrogen. A mixture of this composition when tested failed three times to propagate flame, but on five occasions flame travelled throughout the length of the tube. The flames travelled very slowly and were only visible when the room was in complete darkness.

Upper limit. Hydrogen, per cent.	Result.
63·5	Rapidly moving flame throughout.
64·5	,, ,, ,,
65·0	,, ,, ,,
65·3	,, ,, ,,

With mixtures containing 66 per cent. or more of hydrogen a sharp report occurred on sparking, due to the rapid combustion of a mixture made poorer in hydrogen by diffusion between the point of ignition and the open end of the tube. Flame also travelled rapidly over short distances towards the closed end of the tube ; thus, with 67·5 per cent. hydrogen the flame travelled 25 cm., and with 67·8 per cent. 10 cm. With 68 per cent. no flame could be

Attention should be directed to the slow speed, 8·3 cm. per second, at which flame could travel in a mixture of hydrogen and air at the lower limit, a fact which illustrates the well-known persistence of hydrogen flames. In conformity with the results obtained for other gases, it was expected that the flame in the higher-limit mixture would be equally slow. The fact that so high a speed as 50 cm. per second was recorded was due to the difficulty experienced in igniting the mixture before diffusion at the mouth of the tube could decrease the percentage of hydrogen there.

The coal-gas was made at the carbonising plant of the Experimental Station, and was not diluted with water-gas. The analyses of the two samples were:

	Sample A. Per cent.	Sample B. Per cent.
Benzene and higher olefines	1·2	1·6
Carbon dioxide	0·1	nil
Ethylene	2·9	2·8
Carbon monoxide	7·3	7·1
Hydrogen	50·6	47·0
Methane and higher paraffins	32·9	38·0
Nitrogen (by difference)	5·0	3·5

It will be seen that the difference between the two samples of gas lay almost entirely in the proportions of hydrogen and paraffins that they contained; and from a comparison between the speed—percentage curves for coal-gas A and the hydrogen—methane mixture given in Fig. 1, it is evident that the slower speed of flame obtained with coal-gas B as compared with coal-gas A is due to the higher methane-content of the former. For the highest speed obtainable with the hydrogen—methane mixture, which contained 50 per cent. of each constituent, is considerably slower than the highest speed obtainable with coal-gas A, which also contained 50 per cent. of hydrogen, but only 33 per cent. of methane.

The results obtained on the propagation of flame in horizontal glass tubes of smaller internal diameter than 9 mm. are recorded in the tables that follow. The determinations were made in the same manner, and the numbers in the table have the same significance, as in the experiments with methane and air (*loc. cit.*, p. 658), with which they should be compared.

observed to travel away from the open end of the tube. These results place the upper limit for self-propagation of flame between 65·3 and 66·0 per cent. hydrogen. The determination was completed as follows:

Hydrogen, per cent.	Result.
65·9	Flame travelled rapidly about 40 cm.
65·7	,, ,, ,, ,,
65·6	Complete propagation of flame. ,,

TABLE I.

Coal-gas, Sample A.

Internal diameter of tube, mm.	Coal-gas in mixture. Per cent.								
	12·4	13·1	16·4	17·5	18·4	19·2	20·0	22·7	24·5
2·0	nil	nil	nil	nil	nil	nil	nil	nil	nil
3·0	(25)	(50)	—	—	81·3	—	—	nil*	—
4·2	(25)	49·6	—	—	87·3	—	—	nil*	—
5·0	(30)	53·5	—	—	98·1	—	—	35·3	—
6·0	(44)	55·5	—	—	99·1	—	—	40·6	nil*
7·1	(52)	58·7	86·8	97·7	103·7	102·7	90·3	50·6	nil*
8·0	(60)	59·2	87·4	98·8	104·2	103·9	91·8	57·0	29·8

TABLE II.

Coal-gas, Sample B.

Internal diameter of tube, mm.	Coal-gas in mixture. Per cent.				
	13·1	14·0	14·8	16·5	16·8
2·0	nil	nil	nil	nil	nil
3·0	nil	—	60	—	—
4·2	(35)	—	—	—	—
5·0	(35)	—	—	—	—
6·0	(41)	—	—	—	—
7·1	(52)	62·2	71·4	84·1	80·1
8·0	(57)	63·2	77·4	85·8	82·3

TABLE III.

Hydrogen–Methane, 1:1.

Internal diameter of tube, mm.	Hydrogen–methane in mixture. Per cent.										
	8·45	9·45	11·90	13·90	14·35	14·95	15·95	17·20	18·10	18·65	19·55
2·0	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil
3·0	—	—	56·3	74·9	—	74·5	73·0	nil*	—	—	—
4·2	—	nil	57·9	75·9	—	—	—	46·1	nil*	—	—
5·0	—	(28)	59·4	83·1	—	86·0	84·0	53·5	nil*	—	—
7·1	(30)	38·7	63·0	85·1	88·0	95·8	94·1	74·1	43·3	nil*	—
8·0	(40)	39·4	69·5	87·1	90·7	—	—	75·8	49·4	34·2	nil*

* Flame travelled towards the open ends of the tubes, a distance of 3 cm.

The results recorded in table III are shown as smoothed curves in Fig. 2, which illustrates the extent to which the "limits" are dependent on the environment of the inflammable mixture. It will be seen that the range of mixtures over which continued (horizontal) propagation of flame was possible became gradually restricted as the diameter of the tube was decreased, until with a

C* 2

3 mm. tube it was less than half of that obtaining in a 9 mm.
tube.

With a tube 2 mm. in diameter, no flame could travel away
from the point of ignition, whatever the percentage of combustible
gas present, an observation that applies also to the mixtures of
coal-gas and air. With all mixtures of methane and air, a
diameter of 3·6 mm. prevented the propagation of flame; whereas
with hydrogen and air (30 per cent. hydrogen), Mallard and Le
Chatelier (*Ann. des Mines*, 1883, [viii], **4**, 320) have recorded the
propagation of flame in a glass tube only 0·9 mm. in diameter.

Complementary to these results are the results of experiments

Fig. 2.

Combustible gas in air. Per cent.
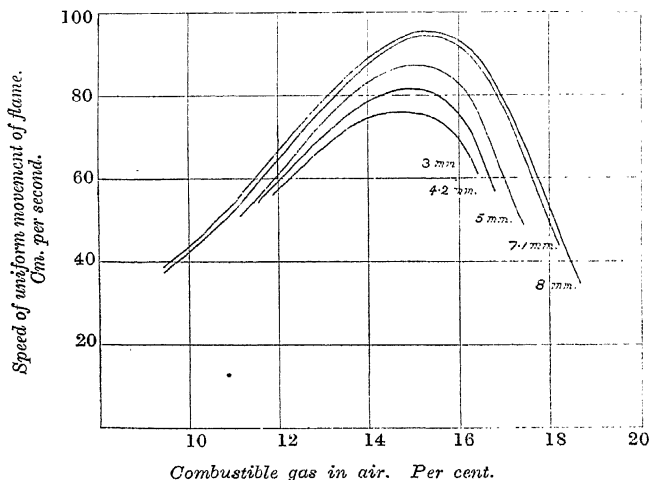
made on the passage of flame in mixtures of coal-gas and air
through brass tubes, either open at both ends or arranged as
extensions to a larger vessel, at the closed end of which the mix-
ture was ignited. It is unnecessary to give the details of these
experiments, which were conducted in the same manner and ex-
hibited the same general features as the experiments with methane.
It is sufficient to record that the flame in an 18 per cent. mixture
of coal-gas *B* and air passed through 15—18 cm. length of brass
tube of 4·4 mm. internal diameter placed horizontally and open
at both ends, and was projected from a closed vessel (20 cm. long)
through 13—15 cm. length of the same brass tubing. The corre-

sponding distances when a 10 per cent. mixture of methane and air was used were 7·5 and 3—4 cm. respectively.

The general conclusion to be drawn from these experiments as regards the testing of miners' safety-lamps is that "coal-gas" is an unsuitable gas to employ for that purpose, for the following reasons:

(1) Comparatively small variations in the composition of coal-gas affect the speed at which flame can travel in its mixtures with air. In particular, a reduction in the proportion of paraffins which it contains, such as is usually accompanied by an increase in the proportion of hydrogen when, as generally, carburetted water-gas is employed to dilute the coal-gas, enables a much higher speed of flame to be attained than can be given by mixtures of methane and air.

(2) Even with gas produced solely by the carbonisation of coal at normal retort temperatures, the speed of propagation of flame attainable is more than double that possible in mixtures of methane and air.

(3) It would seem that the ability of flame to pass through tubes or holes of small diameter is not dependent alone on its speed, although this is the main factor, but is to a certain extent a quality of the inflammable gas concerned. Flame in mixtures of hydrogen and air possesses the property of being able to pass through holes of very small diameter, and the presence of hydrogen in coal-gas confers this property in a certain degree on the flame in mixtures of the latter with air.

ESKMEALS,
 CUMBERLAND.   [*Received, October 30th, 1918.*]

III.—*Mixtures of Nitrogen Peroxide and Nitric Acid.*

By WILLIAM ROBERT BOUSFIELD, K.C.

NITRIC acid and nitrogen peroxide are mutually soluble in certain proportions, and in other proportions give rise to a double layer. When to the simple binary mixture water is added, a more complex mixture arises. A systematic study of these mixtures was projected, beginning with the simple binary mixture and passing on to consider the modifications which are introduced by the addition of water. The present communication deals with the first

part only of this research. The nitric acid and nitrogen peroxide for the research have been specially prepared by Nobel's Explosives Co., Ltd., with whose chief research chemist, Mr. Rintoul, I have been in consultation from time to time.

Nitrogen Peroxide.—Nitrogen peroxide absorbs moisture readily, and in the absence of excess of nitric acid appears to decompose according to the equation

$$N_2O_4 + H_2O = HNO_2 + HNO_3.$$
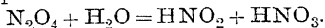
The presence of a very small quantity of water will therefore change the colour of liquid nitrogen peroxide to a dirty green, but traces of moisture may involve the presence of nitrogen trioxide without noticeable change of colour. Two samples of liquid nitrogen peroxide were supplied by Messrs. Nobel. Nearly all the work was done with sample No. 1, which was subsequently found to have contained traces of nitrogen trioxide. Sample No. 2 had been purified by distilling it with phosphoric oxide. The probable reactions which result in this purification appear to be

$$2HNO_3 + P_2O_5 = 2HPO_3 + N_2O_5,$$
$$N_2O_5 + N_2O_3 = 2N_2O_4.$$
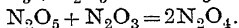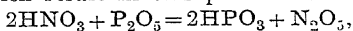
This sample, No. 2, may be regarded as pure liquid nitrogen peroxide.

In the meantime, before receiving this pure sample, I had used up sample No. 1 in nitric acid solutions and recovered it by distillation and rectification with a pear still-head. This sample, to which I may refer as No. 3, appears by the density given below to be nearly as pure as No. 2. This is probably due to the oxidation of the nitrogen trioxide by nitric acid, according to the equation

$$2HNO_3 + N_2O_3 = 2N_2O_4 + H_2O.$$
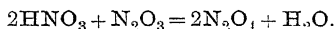
Thus with excess of nitric acid and very little water the reaction

$$N_2O_4 + H_2O = HNO_2 + HNO_3$$
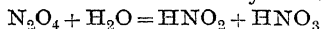
appears to be reversed, and in the presence of excess of nitric acid the water appears to have no decomposing effect on the nitrogen peroxide.

As further evidence of this, the addition of a few drops of water to the orange-coloured liquid nitrogen peroxide turns it a dirty dark green, presumably due to the mixture of the blue nitrogen trioxide or nitrous acid with the orange nitrogen peroxide, but the addition of a few drops of nitric acid destroys the green and restores the orange colour.

The green colour cannot be eliminated by simple rectification, as the nitrogen trioxide and peroxide appear to pass off together, the resulting gas being of a somewhat deeper red colour than that of pure nitrogen peroxide. Nor does the addition of syrupy phos-

phoric acid help matters. Solid phosphoric oxide appears to be necessary to get rid of the nitrogen trioxide unless excess of nitric acid is added.

Another sample (No. 4), of a bulk of about half a litre, which had been accidentally contaminated with sufficient water to turn it to the dark green colour, was mixed with sufficient nitric acid to restore the orange colour and then distilled with phosphoric oxide. The resulting sample, No. 5, was of the same colour and density as the pure sample, No. 2. In the rectification of sample No. 4, the first few c.c. passed over green at a temperature at the top of the still-head of 19—20°. The bulk, which constitutes sample No. 5, distilled at 21·9±0·1°, which may be taken as the boiling point of pure liquid nitrogen peroxide.

TABLE I.

Specific Volumes of Samples of Nitrogen Peroxide.

	4°.	11°.	18°.
No. 1	0·67390	0·68110	0·68864
No. 2	0·67435	0·68172	0·68938
No. 3	0·67432	0·68168	0·68935
No. 4	—	—	0·68946
No. 5	—	0·68170	—

A set of density observations on sample No. 1 was taken at the temperatures given in table II, which gives the observed specific volumes and those calculated from the formula

$$v = 0·66994 + 0·0009767t + 0·00000344t^2.$$

TABLE II.

Specific Volumes of Sample No. 1 at Various Temperatures.

t.	D.	v observed.	v calculated.	Differei
0·08°	1·49250	0·67002	0·67002	±
7	1·47704	0·66703	0·67695	−8
11	1·46822	0·68110	0·68110	±
15	1·45909	0·68536	0·68536	±
18	1·45214	0·68864	0·68863	−1
20	1·44750	0·69085	0·69085	±

For the pure sample No. 2 the specific volume—temperature curve derived from the three duplicated observations at 4°, 11°, and 18° is

$$v = 0·67027 + 0·0010075t + 0·000003t^2,$$

which may be taken as giving the correct specific volume of pure nitrogen peroxide at temperatures from 0° to 20° within ±2 in the fifth place of decimals

Nitric Acid.—The nitric acid used was specially purified and sent to me by Messrs. Nobel with the following analysis:

Nitric acid	99·68	per cent.
Hydrochloric acid	0·007	,, ,,
Sulphuric acid	0·068	,, ,,
Nitrous acid......................	0·012	,, ,,
Mineral matter	nil	
	99·767	,, ,,

I have taken the percentage of water by difference as 0·233 per cent.

The densities of this acid at the temperatures indicated are:

4°.	11°.	18°.
1·5381	1·5254	1·5126

In calculating the strength of the various mixtures of nitric acid and nitrogen peroxide, to which reference is made later, the nitrous acid given in the above analysis has been reckoned as nitrogen peroxide, since, for the reasons above given, it is assumed that with very concentrated nitric acid the nitrous acid present is oxidised to give nitrogen peroxide and water.

In table III are given the resulting values of the specific volumes, derived from the density determinations.* P is the percentage by weight of nitrogen peroxide in the mixture. The temperature coefficients, α, from 4° to 11° and from 11° to 18°

TABLE III.

Specific Volumes of Mixtures of Nitric Acid and Nitrogen Peroxide.

				Temperature-coefficients.	
				4—11°	11—18°
P.	v_4.	v_{11}.	v_{18}.	$\alpha \times 10^5$.	$\alpha \times 10^5$.
0	0·65015	0·65557	0·66113	77	79
1·2168	0·64839	0·65374	0·65920	76	78
8·021	0·63719	0·64211	0·64715	70	72
16·88	0·62372	0·62821	0·63291	64	67
26·09	0·61214	0·61655	0·62113	63	65
34·925	0·60445	0·60885	0·61346	63	66
37·60	0·60296	0·60743	0·61204	64	66
42·01	0·60112	0·60568	0·61044	65	68
43·71	0·60082	0·60543	0·61026	66	69
46·70	0·60088	0·60561	0·61059	68	71
48·66	0·60113	0·60599	0·61110	69	73
49·96	0·60145	0·60639	0·61161	71	75
51·37	0·60205	0·60715	0·61248	73	76
53·10	0·60341	0·60873	0·61436	76	80
93·86	—	—	0·68610	—	—
96·93	0·67305	0·68030	0·68786	104	108
98·49	0·67371	0·68098	0·68855	104	108
100·00	0·67435	0·68172	0·68938	105	109

* The actual density determinations have been omitted at the request of the Publication Committee to save space.

TABLE IV.

Contraction of Mixtures of Nitric Acid and Nitrogen Peroxide.

	Contraction per c.c. of solution.			Contraction per gram of solution.		
P.	4°.	11°.	18°.	4°.	11°.	18°.
1·22	0·0032	0·0033	0·0034	0·0021	0·0022	0·0023
8·02	0·0234	0·0242	0·0251	0·0149	0·0156	0·0163
16·88	0·0489	0·0506	0·0521	0·0305	0·0318	0·0330
26·09	0·0724	0·0743	0·0763	0·0443	0·0458	0·0474
34·92	0·0896	0·0917	0·0938	0·0542	0·0559	0·0575
37·60	0·0934	0·0954	0·0976	0·0563	0·0580	0·0597
42·01	0·0985	0·1005	0·1025	0·0592	0·0609	0·0626
43·71	0·0997	0·1017	0·1036	0·0599	0·0616	0·0632
46·70	0·1008	0·1027	0·1044	0·0606	0·0622	0·0637
48·66	0·1011	0·1028	0·1044	0·0608	0·0623	0·0638
49·96	0·1011	0·1026	0·1040	0·0608	0·0622	0·0636
51·37	0·1005	0·1019	0·1031	0·0605	0·0619	0·0632
53·10	0·0988	0·0998	0·1005	0·0596	0·0607	0·0618
93·86	—	—	0·0023	—	—	—
96·93	0·0008	0·0009	0·0009	—	—	—
98·49	0·0004	0·0005	0·0006	—	—	—

are also set out in table III, as they give an important clue to the nature of the combination which is taking place in the mixture.

Another important matter bearing on this is the contraction which takes place at various constitutions of the mixture. The euthetic point, that is, the point of closest packing (see Bousfield, T., 1915, **107**, 1412), may be obtained by calculating the ratio of the volume of the constituents before mixture to the volume at the same temperature after mixture, which is

$$R \qquad \frac{Pv_0 + (100 - P)w}{100v},$$

where $v_0 =$ specific volume of nitrogen peroxide, $w =$ specific volume of nitric acid, $v =$ specific volume of the mixture.

It should be noted that $R - 1$ is the contraction per c.c. of solution formed, the values of which are set out in table IV.

In the same table are set out the values of the difference between the volume of a gram of the constituents before mixing and the volume after mixing, which is

$$\Delta = \frac{Pv_0 + (100 - P)w}{100} - v.$$

Consideration of the Results.—The results given in the tables are exhibited in Figs. 1, 2, 3, and 4, where they are set out on the values of P, the percentage by weight of nitrogen peroxide, as abscissæ. There are shown in:

Fig. 1, the specific volumes of the mixtures.
Fig. 2, the values of $R-1$ near the maximum.
Fig. 3, the values of Δ near the maximum.
Fig. 4, the temperature coefficients for the intervals 4—11°
11—18°.

FIG. 1.
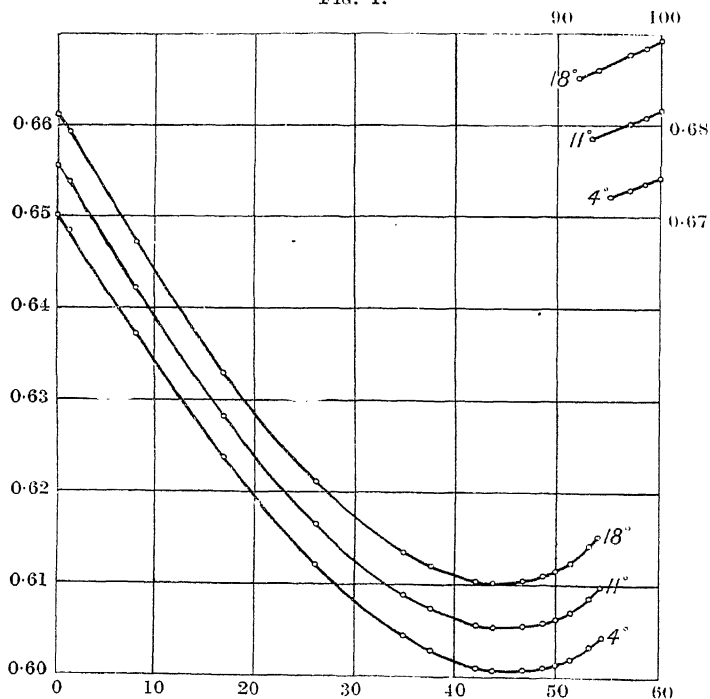
Specific volume of mixtures of nitric acid and nitrogen peroxide at
4°, 11° and 18°.

$x = $ Percentage of nitrogen peroxide.
$y = $ Specific volume.

The notable heat of evolution on mixing approximately equal
weights of nitric acid and nitrogen peroxide (which it is proposed
to determine accurately at a later stage) indicates a powerful com-
bination.   The minimum values of the specific volume curves give
the same indication, showing a notable contraction of about 10

per cent.   The minima do not, however, locate the exact composition.   They occur:

for   4° at about 44·6 per cent.
for 11°   ,,   44·2   ,,
for 18°   ,,   43·8   ,,

Fig. 2.

Contraction per c.c. of solution.

$$x = P.$$
$$y = R - 1.$$
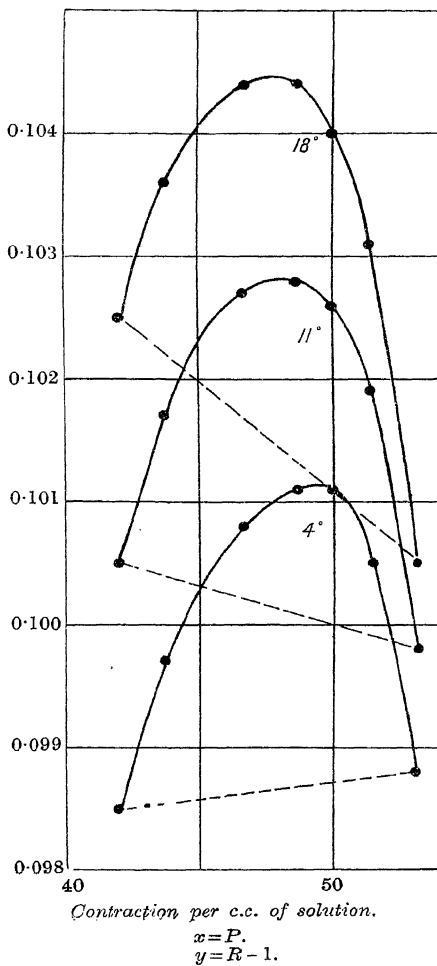
The position of the minimum is so largely determined by the mere density differences of the two components that it cannot locate precisely the percentage of the combination.

The euthetic point (see Bousfield, *loc. cit.*) is generally very close to the neighbourhood of the point of definite composition. The

FIG. 3.

Contraction per gram of solution.

$$x = P.$$
$$y = \triangle.$$
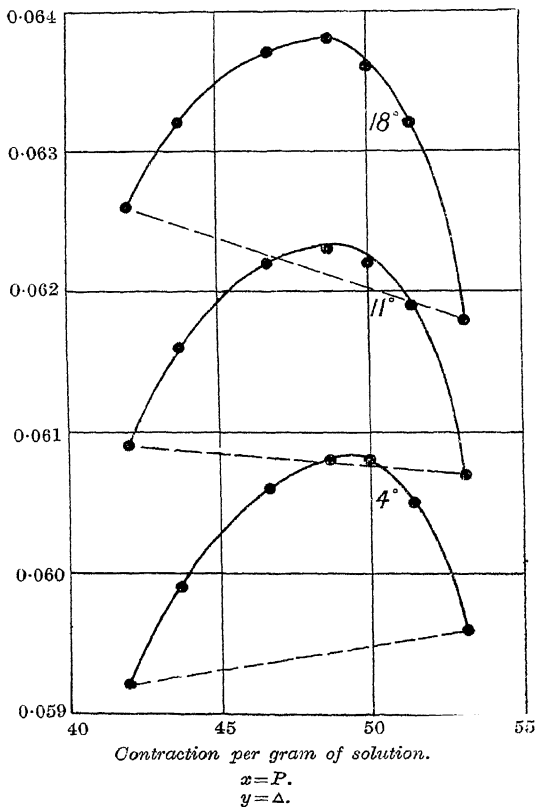
values of the contraction per c.c. of solution which determine the euthetic point are given in table IV and set out in Fig. 2. The maxima correspond with the euthetic point, and occur:

for   4° at about 49·2 per cent.
for 11°   ,,   48·4   ,,
for 18°   ,,   47·6   ,,

The actual position of the euthetic point is determined, not only by contraction due to combination, but also by contraction due to changes in the polymerisation of the constituents. The high temperature coefficients for both constituents indicate that these changes are notable. The percentage 49·2 at 4° corresponds very nearly with the composition $3HNO_3,2N_2O_4$.

If we take the curves in Fig. 3, in which the values of the contraction per gram of solution are set out, the effect of polymerisation is to some extent excluded, and the maxima for 4° and 11° appear to occur at 49·3 per cent., whilst that for 18° is again shifted slightly to the left. On the whole, then, it may be said

FIG. 4.
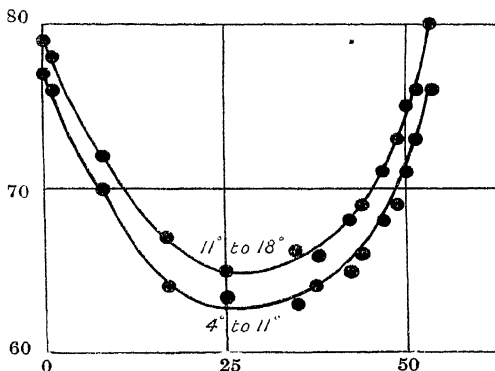
Temperature-coefficients of specific volumes of mixtures of nitric acid and nitrogen peroxide.

$x = P.$
$y = Temperature\text{-}coefficient\ a.$

that the indications point to the composition of the definite compound $3HNO_3,2N_2O_4$, which corresponds with 49·33 per cent.

An inspection of Fig. 4, in which the temperature coefficients are set out, shows a definite minimum at 26·7 per cent., which appears to be the same for each range of temperature; this corresponds with the definite composition $4HNO_3,N_2O_4$. The first part of the specific volume curve shown in Fig. 1 is approximately straight, which indicates that the whole of the nitrogen peroxide added up to about 15 per cent. enters into this combination with nitric acid. Furthermore, the proportions of nitric acid and the compound, $4HNO_3,N_2O_4$, derived from the mass-action relation give a calculated specific volume which corresponds closely with

the actual specific volume curve for a considerable distance, that is, until the effect of the increasing proportion of the still denser combination becomes sensible. On the whole, we may conclude that at least two definite compounds exist in the solutions, namely, $4HNO_3,N_2O_4$ and $3HNO_3,2N_2O_4$.

The Composition of the Double Layers.—The specific volume curves have a gap between about 54 and 92 per cent. If at 4—18° a mixture between these limits is made, the solution separates into two layers, which are mutually saturated.

Nitrogen peroxide is soluble in nitric acid up to about a 54 per cent. solution, but the solubility of nitric acid in nitrogen peroxide is very much less. In order to determine the maximum solubilities at different temperatures, the two components were shaken together from time to time at the required temperatures, forming a cloudy liquid, and kept in a thermostat until the two clear layers were completely separated. The different layers were then drawn off into a pyknometer at the required temperatures, and again kept in the thermostat at these temperatures during the adjustment of the pyknometer. The resulting density determinations enabled the compositions to be determined.

In table V are given the density observations for saturated solutions of nitric acid in nitrogen peroxide, together with the specific volumes at the temperatures and the resulting percentage, p, of nitric acid in the saturated solutions.

TABLE V.

Saturated Solutions of Nitric Acid in Nitrogen Peroxide.

	D.	v.	Percentage of nitric acid.
4°	1·48742	0·67231	4·90
11	1·47351	0·67865	6·67
18	1·45940	0·68521	8·05

Since at this end of the specific volume curves they are practically straight lines, the percentages are easily calculated from the formula

$$v_0 - v_t = \beta p,$$

where v_0 = specific volume of nitrogen peroxide, v_t = specific volume of solution containing p per cent. of nitric acid, the values of the constants being:

	4°.	11°.	18°.
	0·67435	0·68172	0·68938
β	0·000424	0·000476	0·000526

It will be observed that the solubility of nitric acid in nitrogen peroxide rises rapidly with temperature, being about doubled in

the range from $0°$ to $20°$. The values indicate that the solubility would vanish at about $-10°$.

In table VI are given the density observations for saturated solutions of nitrogen peroxide in nitric acid, together with the specific volume at the temperatures and the approximate percentages of nitrogen peroxide in the saturated solutions.

TABLE VI.

Saturated Solutions of Nitrogen Peroxide in Nitric Acid.

	D.	v.	P.
$4°$	1·65432	0·60448	54·4
11	1·63942	0·60997	54·3
18	1·62501	0·61538	54·0

In this case, the approximate compositions are determined diagrammatically from a large-scale specific volume curve.. The temperature of my laboratory in the end of May when these last observations were taken made them very difficult. It is, however, clear that the change of solubility with temperature is in this case very small, and it appears to diminish with rising temperature.

St. Swithin's,
    Hendon, N.W.   [*Received, August 29th,* 1918.]

IV. —*The Effect of Dilution in Electro-titrimetric Analyses.*

By Gilbert Arthur Freak.

The first application of conductivity measurements to analysis is that due to Küster and Grüters (*Zeitsch. anorg. Chem.*, 1903, **35**, 454), who showed that acids could be titrated accurately by these means. Later, Küster, Grüters, and Geibel (*ibid.*, 1904, **42**, 225) proved the accuracy of the method even when such substances as potassium dichromate and potassium permanganate were present in the acid solution. The estimation of acetic acid in vinegar, of total acid in red wine, of magnesia, and of various alkaloids was also shown to be possible.

Further work has demonstrated that the method is capable of very varied application. Amongst the uses to which it has been put may be noticed the analysis of wines by Duboux (*Chem. Zeit.*, 1913, **37**, 879) and by Duboux and Dutoit (*Compt. rend.*, 1908,

147, 134), the preparation of neutral ammonium citrate solutions
by Hall (*J. Ind. Eny. Chem.*, 1911, **3**, 559), and the analysis of soil
solutions by Van Suchtelen and Itano (*52nd Ann. Rep. Mich.
Board of Agric.*, 1913, 49). The last-named workers have also pub-
lished (*J. Amer. Chem. Soc.*, 1914, **36**, 1793) the results of experi-
ments on the estimation of chlorides, sulphates, nitrates, phosphates,
potassium, calcium, ferrous iron, strong and weak acids, and of
chlorides and phosphates in urine. Quite recently, Harned (*J.
Amer. Chem. Soc.*, 1917, **39**, 252) has shown that certain bivalent
metals in the form of their sulphates can be determined accurately
by the conductivity method by titration with barium hydroxide.
Meerburg (*Versl. v. h. Centr. Lab. t. b. h. v. h. Staatsoez. o. d.
Volksgehondh.*, 44–54, 1917; *Chem. Weekblad*, 1917, **14**, 1054) has
reported adversely on the method as applied to the estimation of
sulphates by barium acetate and of calcium by oxalic acid, but
mentions that good results may be obtained in the determination of
alkalinity in potable waters.

It is noteworthy that, although the method has been applied to
so many reactions, no attention has been paid to the lower limit
of concentration at which accuracy may still be obtained. Most of
the experiments have been carried out on relatively concentrated
solutions (seldom weaker than $0·1N$), the only reference to results
with very dilute solutions being one by Van Suchtelen and Itano
(*loc. cit.*), who state that the titration of as little as 5 c.c. of
$0·001N$-sulphuric acid with $0·01N$-sodium hydroxide can be per-
formed accurately. In those titrations involving the precipitation
of a salt, the solubility of which would be expected to limit the
sensitiveness of the method, this point has not been touched upon.

It appears, therefore, to the author that an investigation of this
nature was desirable. If the method is capable of yielding accurate
results at very low concentrations, many estimations, for example,
those carried out in the analysis of potable waters, could be made
without previous concentration of the solutions. The present com-
munication is concerned with the limits of the method as applied
to the estimation of sulphates, chlorides, calcium, and magnesium.
Rigid accuracy was not aimed at, the object being to find to what
extent the method could compete with ordinary gravimetric or
volumetric processes without the introduction of troublesome pre-
cautions. To that end, beyond the use of standardised measuring
vessels and of " purest " commercial reagents, no special precautions
were taken. No attempt was made to keep the temperature of the
solutions constant during the titrations, the duration of which was
usually fifteen to twenty minutes.

Except for the use of a double receiver telephone, which proved very convenient in minimising the interference of external noises, the apparatus employed was of the usual nature and therefore calls for no special comment.

The liquid to be titrated was placed in a beaker of such a size that thorough mixing could be effected by giving the vessel a rotatory motion, the stationary electrodes serving as a stirrer. The reagent was delivered from a burette capable of being read to 0·01 c.c. The curves were plotted with conductivity as ordinates and volume

FIG. 1.

C.c. $N/10$-BaCl$_2$.
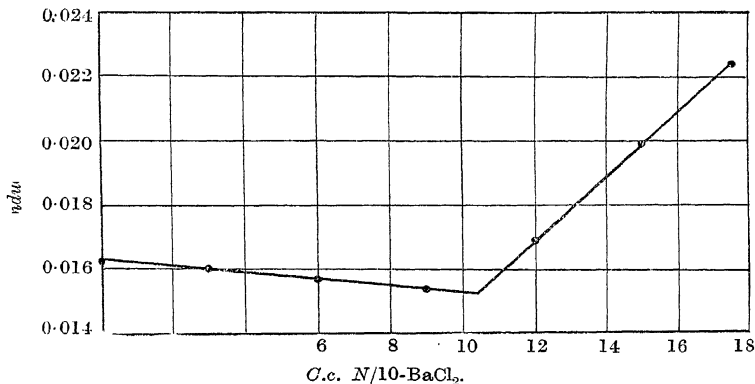
of reagent as abscissæ, and in order to eliminate experimental errors at least three, and usually more, readings were taken on each limb of the curve.

Estimation of Sulphates.

A stock solution of Merck's purest potassium sulphate was prepared and the SO$_4$ estimated gravimetrically in duplicate as barium sulphate. From this solution weaker solutions were prepared by dilution. For the titration of these, two solutions of barium chloride, approximately $N/10$ and $N/25$ respectively, were prepared and similarly standardised.

Table I shows that the results are accurate only down to a concentration of about 200 milligrams of SO$_4$ per litre, a typical curve being shown in Fig. 1. When the concentration of SO$_4$ is 100 milli-

grams or less per litre, the precipitation of barium sulphate is so incomplete that the resulting curve changes entirely in character, exhibiting irregularity, but no definite break such as appears in Fig. 1.

Van Suchtelen and Itano (*loc. cit.*) added to their solutions a certain amount of the salt that was to be precipitated with the object of avoiding errors due to solubility. In order to test this procedure, a suspension of fine precipitated barium sulphate in distilled water was added to the sulphate solution in the beaker some little time prior to titration. The results are given in Table II.

TABLE I.

Concentration of SO_4, mg. per litre.	Strength of $BaCl_2$.	SO_4 found. Per cent.
990	$N/10$	100·0, 100·4, 99·4
198	,,	99·2, 99·2, 99·2
99	,, $\left.\begin{array}{c} \\ \end{array}\right\}$	No end-point.
49·5	$N/25$	

TABLE II.

Concentration of SO_4, mg. per litre.	Strength of $BaCl_2$.	SO_4 found. Per cent.
99	$N/10$	99·7, 99·7
49·5	$N/25$	99·5, 99·2, 99·6
24·7	,, $\left.\begin{array}{c} \\ \end{array}\right\}$	End-point indefinit
9·9	,,	

Reference to table II will show that this method succeeded to a certain extent as, by means of it, good results were obtained down to a concentration of about 50 milligrams of SO_4 per litre. However, it was not effective when only 25 milligrams of SO_4 per litre were present, giving curves with an indefinite end-point of the type shown in Fig. 2. Titration at boiling temperature did not alter the character of this curve. In such cases it is possible, by taking only those points well remote from the curved portion, to arrive at an approximate value for the end-point (see dotted lines). For instance, figures derived in this manner from experiments on solutions containing 25 milligrams of SO_4 per litre were about 5 per cent. in excess of the correct value.

Estimation of Chlorides.

The salt chosen for this purpose was a sample of Merck's purest fused sodium chloride. A stock solution of this, together with the approximately $N/10$- and $N/25$-silver nitrate solutions used for titration, was standardised by duplicate gravimetric estimations as silver chloride.

The results obtained with varying concentration of chlorine are shown in table III.

TABLE III.

Concentration of Cl, mg. per litre.	Strength of AgNO₃.	Cl found. Per cent.
1000	$N/10$	99·7, 99·3
200	,,	100·1, 99·3, 100·8
50	$N/25$	100·2, 100·9
10	,,	100·6, 100·8
5	,,	End-point indefinite.

. As in the case of sulphates, a limit of concentration is reached at which the method fails, the figure in this instance being 10 milli-

FIG. 2.

C.c. $N/25$-BaCl₂.
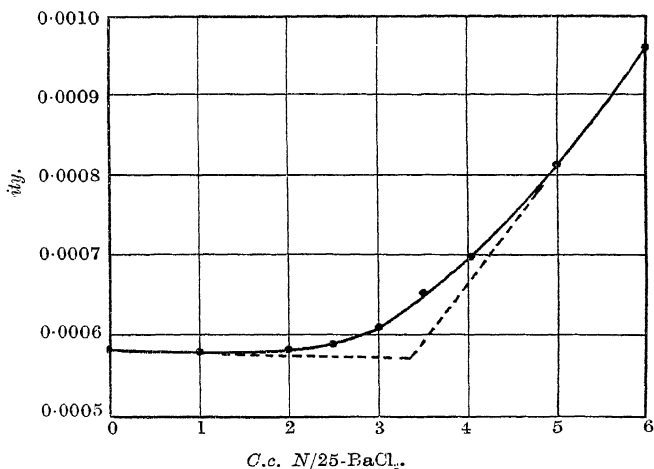
grams of chlorine per litre. The addition of precipitated silver chloride before titration did not render the end-point sharp at lower concentrations.

The type of curve obtained in this estimation is similar to that shown in Fig. 1.

Estimation of Calcium.

A stock solution of calcium chloride was prepared by dissolving pure calcite in hydrochloric acid and eliminating the excess of acid by repeated evaporations on the water-bath. Both this solution and the approximately $N/10$-ammonium oxalate solution employed

in the titrations were standardised by means of potassium perman-
ganate.

Table IV shows the results obtained.

TABLE IV.

Concentration of Ca, mg. per litre.	Ca found. Per cent.
500	100·0, 100·4, 99·2, 100·4
200	99·1, 100·6, 99·1
100	End-point indefinite.

As in the case of the determination of chlorides, previous addi-
tion of the precipitated salt did not lead to sharp end-points at the
last-mentioned concentration.   In three such experiments, figures
given by producing the straight portions of the curves gave 97·0,
97·6, and 95·8 per cent. respectively of the amounts taken.

Estimation of Magnesium.

A solution of Merck's purest magnesium sulphate was employed,
standardisation being effected by duplicate estimations as mag-
nesium pyrophosphate.   An approximately $N/10$-sodium hydroxide
solution, standardised by means of sulphuric acid and pure sodium
carbonate, was used for titration.

Variation of the concentration of magnesium gave results shown
in table V.   The typical curves for these cases have no minimum,
but exhibit a definite break.

TABLE V.

Concentration of Mg, mg. per litre.	Mg. found. Per cent.
539	99·2, 99·7, 99·7
· 269·5	99·7, 100·1, 100·4, 100·1
202	100·8, 99·9, 100·8, 100·6
134·5	End-point indefinite.

Addition of magnesium hydroxide prior to titration lead to no
improvement at the last-mentioned concentration.

In connexion with the estimation of magnesium by this method
it is interesting to note that Harned (*loc. cit.*) says, "This titra-
tion gives only a fairly easily detectable end-point for the change in
direction of the plot before and after the end-point is not great.   A
reagent must, therefore, be sought which will increase the difference
in the slopes at the end-point."   For this reason he employed
barium hydroxide to titrate solutions containing magnesium sul-
phate.   Apart from the fact that the use of this reagent, to be

effective, demands that the magnesium shall be present as sulphate and the total elimination of carbon dioxide from the solution, comparison of Harned's figures with those recorded above shows that the use of barium hydroxide does not present any definite advantage. It appears that errors from other sources are of greater magnitude than that derived from difficulty in reading the intersection of the two limbs of the curve.

Summary of Results.

(1) The determination, by means of conductivity measurements, of sulphates, chlorides, calcium, and magnesium has been studied at low concentrations.

(2) It has been shown that, in relatively weak solutions, very small quantities of each of the above mentioned may be estimated, without any attempt at temperature control, with an error not exceeding ±1 per cent.

(3) In each case a limit of dilution is reached at which the results cease to be accurate, smooth conductivity curves being obtained. With the exception of the case of sulphate estimations, saturation of the solution with the salt to be precipitated does not lead to an improvement in this respect.

V.—The Optically Active neoMethylhydrindamines.

By (the late) LT. JOSEPH WALTER HARRIS.*

THE reduction of β-methyl-α-hydrindoxime, $CH_2 {<}{{CHMe}\atop{C_6H_4}}{>}C{:}NOH$,

with sodium amalgam and acetic acid leads to the formation of two

* Lt. J. W. Harris, B.Sc., was one of those who, actuated by a high sense of patriotic duty, joined the O.T.C. of the University College, Nottingham, before there was any immediate prospect of a war, and his efficiency and enthusiasm led to his promotion to the rank of colour sergeant. In the summer of 1914 he had just completed his first piece of research work and when war was declared he immediately volunteered for active service. Shortly afterwards he was given a commission in the 3rd Lincolns and went to the Western front, where he was killed in action during the early part of the war.

His death was a great blow to all who knew him, whether in civilian or in military life; he was a most promising chemist, an ideal officer. The present

dl-bases, one of which may be isolated by the fractional crystal-
lisation of the hydrochlorides prepared from the mixture (Kipping
and Clarke, T., 1903, **83**, 913). The other base cannot be obtained,
at any rate easily, in this way or by a similar treatment of the
normal sulphates, benzoates, cinnamates, or picrates, but by frac-
tionally crystallising the *d*-bromocamphorsulphonates and mechani-
cally separating the obviously different crystals, both the *dl*-bases
can be ultimately obtained in a state of purity (Tattersall and
Kipping, T., 1903, **83**, 918).

As this method of separation was unsatisfactory, the author of
this paper, at the suggestion of Professor Kipping, made some
further experiments on the subject, and found that the two *dl*-bases
in the crude product could be isolated in the manner described
below. He then succeeded in resolving the *dl-neo*-base into its
optically active components, both of which were obtained in a state
of purity.

All the four optically isomeric β-methylhydrindamines, therefore,
have now been characterised; the two *neo*-bases, which form only
about 25 per cent. of the original mixture, have very low molecular
rotations compared with those of the other two methylhydrind-
amines.

Separation of Methylhydrindamine and neo*Methylhydrindamine*
by means of their Hydrogen Oxalates.

The aqueous solution of the mixed bases obtained by the reduc-
tion of methylhydrindoxime was neutralised with finely divided
oxalic acid, and a further equal quantity of acid was added. This
solution was then concentrated and cooled. The first fraction con-
sisted of tufts of long, silky needles, and was nearly pure methyl-
hydrindamine hydrogen oxalate. Subsequent fractions were simi-
lar, but the needles gradually became less well defined, and when
about two-thirds of the total substance had been separated the
deposits consisted of hard, crystalline masses. The latter, after
several recrystallisations from water, yielded tufts of needle-like
prisms which were *neo*methylhydrindamine hydrogen oxalate. Some
ammonium salts separated in large, transparent masses from time
to time, but these were easily removed by extracting the salt of the
organic base with alcohol. By the above method about five-sixths
of the original mixture was separated into the two *dl*-salts, the pro-

portion being about three to one, methylhydrindamine being present in the larger quantity.

dl-*Methylhydrindamine hydrogen oxalate,*

$$C_{10}H_{11}\cdot NH_2, C_2H_2O_4, H_2O,$$
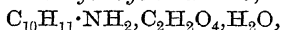
crystallises from water, in which it is readily soluble, in tufts of long, silky needles melting at 110—111°. These are hydrated and lose water at 70—80°; at 100° some decomposition is observed, but this is not noticeable in the melting-point tube. The dehydrated salt melts at 143—145° with slight decomposition :

0·4338 lost 0·031 at 80°. $H_2O = 7\cdot14$.

The above formula requires $H_2O = 7\cdot06$ per cent.

The benzoyl derivative of the base, made in the usual way, crystallised from alcohol in needles melting at 150°, showing the base to be methylhydrindamine (Tattersall and Kipping, *loc. cit.*).

dl-neo*Methylhydrindamine hydrogen oxalate,*

$$C_{10}H_{11}\cdot NH_2, C_2H_2O_4, 2H_2O,$$
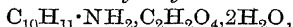
in an impure condition, crystallises in compact masses. From water and alcohol the pure compound is obtained in tufts of needle-like prisms, which partly liquefy at about 100° and finally melt at 173—175°, which is the melting point of the anhydrous salt. When treated with benzoyl chloride, the salt gave a benzoyl derivative, crystallising in needles and melting at 169°, which is the melting point of the benzoyl derivative of *neo*methylhydrindamine (Tattersall and Kipping, *loc. cit.*): *

0·4336 lost 0·0568 at 90°. $H_2O = 13\cdot1$.

The above formula requires a loss of 13·2 per cent.

0·1454 anhydrous salt gave 0·3246 CO_2 and 0·0834 H_2O; $C = 60\cdot8$; $H = 6\cdot4$.

$C_{12}H_{15}O_4N$ requires $C = 60\cdot8$; $H = 6\cdot33$ per cent.

Resolution of dl-neo*Methylhydrindamine.*

dl-neo*Methylhydrindamine hydrogen oxalate* (20 grams) was decomposed with sodium hydroxide, the base distilled in steam, and the distillate neutralised with tartaric acid, a further quantity of the acid being added to form the hydrogen salt. The solution was then concentrated to a small bulk, allowed to cool, and a crystal of pure *l-neo*methylhydrindamine hydrogen tartrate intro-

* Since the melting point of the A-base described by Kipping and Clarke (*loc. cit*) was 169°, it is evident that by the fractional crystallisation of the hydrochlorides of the mixed bases, the salt of *dl-neo*methylhydrindamine is first isolated, whereas in the case of the *d*-bromocamphorsulphonates the salt of *dl*-methylhydrindamine forms the most sparingly soluble fraction.— F. S. K.

duced. A deposit consisting of tufts of needles separated and was collected.   The amount of this fraction was roughly about one-third of the whole.   If the solution was allowed to remain too long before it was filtered, the needle-like crystals became covered with white masses.   This first fraction was recrystallised from water until its melting point became constant and consisted of *l-neo*methylhydrindamine hydrogen tartrate (about 8 grams).   The mother liquors, on further concentration and seeding, gave deposits of white masses, obviously a mixture and melting over a wide range. The last mother liquors gave long, white needles melting at 165°. It was, however, found to be impossible to isolate a pure compound from these mother liquors, owing to the great solubility of the salt.

The whole of the mother liquor was therefore decomposed with sodium hydroxide, the base distilled in steam, and the distillate neutralised with hydrochloric acid.   On concentrating the solution, long needles of *dl-neo*methylhydrindamine separated, but the final mother liquor was found to contain a salt which was more readily soluble in water than that of the *dl*-base, and the solution of this salt showed dextrorotation.

To obtain this dextrorotatory base, the active mother liquor was decomposed with sodium hydroxide, the base distilled in steam, and the solution neutralised with *d*-bromocamphorsulphonic acid.   The solution was concentrated until it became turbid and allowed to remain, when a mass of needles separated.   These were recrystallised from water until the melting point became constant at 229—230°.   This substance was found to be *d-neo*methylhydrindamine *d*'bromocamphorsulphonate.

l-neo*Methylhydrindamine hydrogen tartrate,*

$$C_{10}H_{11} \cdot NH_2, C_4H_6O_6, H_2O,$$
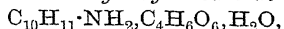
the salt which forms the most sparingly soluble portion described above, crystallises from water or alcohol in large, vitreous prisms, often growing together in leaf-like masses.   It is hydrated, and when heated in a melting-point tube it partly liquefies at about 100° and finally melts at 173°.   It is readily soluble in water, less so in alcohol, and practically insoluble in ethyl acetate, acetone, benzene, or chloroform :

0·3522 lost 0·0204 at 100°. $H_2O = 5·71$.
    The above formula requires $H_2O = 5·71$ per cent.

Samples dried at 100° gave, in a 200 mm. tube in aqueous solution, the following results:

Wt. of salt.	Vol. of solution.		$[a]_D$.	$[M]_D$.
0·7116 gram .	25 c.c.	0·65°	11·4°	34°
0·4600 ,, .		0·42	11·4	34

As the molecular rotation of the tartaric acid ion in its metallic hydrogen salts is $[M]_D$ 42°, that of the base is $[M]_D -8°$.

l-neo*Methylhydrindamine* d-*bromocamphorsulphonate*,

$$C_{10}H_{11}\cdot NH_2,C_{10}H_{14}OBr\cdot SO_3H,$$
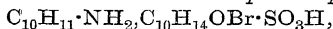
is moderately soluble in water, and crystallises from the warm solution in aggregates of needles, the solution first becoming milky if the salt is not free from the optically active isomeric base. These needles are hydrated, but lose all their water on exposure to the air. The freshly crystallised substance when heated in a melting-point tube partly liquefies at about 80° and finally melts at 214°. It is more readily soluble in alcohol than in water, and easily dissolves in ethyl acetate, chloroform, or acetone, but is insoluble in ether.

The anhydrous salt was examined in aqueous solution in a 200 mm. tube.

Wt. of salt.	Vol. of solution.		$[\alpha]_D.$	$[M]_D.$
0·5068	25 c.c.	2·32°	57·2°	262°
0·3856		1·75	57·1	261

Taking the molecular rotation of the bromocamphorsulphonic acid ion to be $[M]_D$ 270°, these results give a value of $[M]_D -8°$ or $-9°$ for the base.

l-neo*Methylhydrindamine hydrochloride*, $C_{10}H_{11}\cdot NH_2,HCl$, is much more readily soluble in water than the hydrochloride of the *dl*-base, and crystallises from this solvent in long, silky needles. It is very readily soluble in water or alcohol and also dissolves in ethyl acetate or chloroform, but is practically insoluble in ether or carbon tetrachloride. When heated in a melting-point tube, the substance begins to char at about 235°. The air-dried salt is anhydrous.

The following results were obtained in aqueous solution in a 200 mm. tube:

Wt. of salt.	Vol. of solution.	$\alpha.$	$[\alpha]_D.$	$[M]_D.$
0·5250	25 c.c.	$-0·13°$	$-3·1°$	$-5·7°$
0·7986	,,	$-0·23$	$-3·6$	$-6·5$
0·7754	,,	$-0·21$	$-3·4$	$-6·2$

l-neo*Methylhydrindamine* d-*camphorsulphonate*,

$$C_{10}H_{11}\cdot NH_2,C_{10}H_{15}O\cdot SO_3H,$$
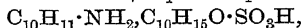
is very readily soluble in water, and crystallises in long, vitreous prisms. The air-dried salt is anhydrous, and when heated sinters at about 210° and finally melts at 220°. It is readily soluble in chloroform, sparingly so in alcohol or acetone, and practically insoluble in ether or ethyl acetate.

The following results were obtained in aqueous solution in a 200 mm. tube:

Wt. of salt.	Vol. of solvent.	α.	$[\alpha]_D$.	$[M]_D$.
0·5898	25 c.c.	0·54°	11·4°	43·2°
0·5282		0·50	11·8	44·7

Taking $[M]_D$ for camphorsulphonic acid as 49°, these results give for the base $[M]_D$ $-5\cdot8°$ and $-4\cdot3°$ respectively.

The *benzoyl* derivative of *l-neo*methylhydrindamine crystallises from aqueous alcohol in long, silky needles melting at 171°.

d-neo*Methylhydrindamine* d-*bromocamphorsulphonate*,

$$C_{10}H_{11}\cdot NH_2, C_{10}H_{14}OBr\cdot SO_3H,$$
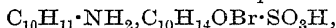
is readily obtained in a pure condition from the active base contained in the mother liquors from the *dl*-hydrochloride (see above). It crystallises from warm water in tufts of fine, silky needles, and, as with many other bromocamphorsulphonates, the warm solution becomes milky when the salt separates unless it is free from its optical isomeride. The freshly crystallised salt contains water, probably one molecular proportion, but it was impossible to obtain accurate determinations on this point, since the salt rapidly loses water in the air and the air-dried salt is anhydrous.

1·69 of the salt, roughly dried in the air, lost 0·544 at 100°. Loss = 3·2, whereas $1H_2O$ requires a loss of 3·1 per cent.

When the freshly crystallised salt is heated in a melting-point tube it partly liquefies at about 100° and finally melts at 229—230°. It is moderately soluble in water, more readily so in alcohol; it is also soluble in acetone or ethyl acetate, but insoluble in carbon tetrachloride or ether.

d-neo*Methylhydrindamine hydrochloride*, $C_{10}H_{11}\cdot NH_2, HCl$, prepared from the pure bromocamphorsulphonate, was dried at 100° and examined polarimetrically in aqueous solution in a 200 mm. tube.

Wt. of salt.	Vol. of solution.		$[\alpha]_D$.	$[M]_D$.
0·5200	25 c.c.	0·13°	3·1°	5·7°
0·4268		0·10	3·0	5·5

d-neo*Methylhydrindamine hydrogen tartrate*,

$$C_{10}H_{11}\cdot NH_2, C_4H_6O_6, H_2O,$$
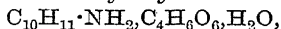
is much more readily soluble in water than the hydrogen tartrate of the *l*-base, and crystallises in aggregates of needle-like prisms:

1·2146 air-dried salt lost 0·0726 at 100°. $H_2O = 5\cdot9$. The above formula requires $H_2O = 5\cdot71$ per cent.

When heated in a melting-point tube the salt sinters at about 90° and finally melts at 166—167°. The following results were

obtained with aqueous solutions of the anhydrous salt in a 200 mm. tube :

Wt. of salt.	Vol. of solution.	a.	$[a]_D$.	$[M]_D$.
0·3122	25 c.c.	0·40°	16·0°	47·5°
0·3328		0·43	16·2	48·1

Taking the molecular rotation of the tartaric acid ion in its hydrogen salts as $[M]_D$ 42°, these results give $[M]_D$ 5·5° and 6·1° respectively for the base.

d-neo*Methylhydrindamine* d-*camphorsulphonate*,

$$C_{10}H_{11}\cdot NH_2, C_{10}H_{15}O\cdot SO_3H,$$
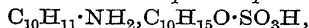
crystallises from water in felted masses of needles which melt and decompose at 195—205°. The salt is extremely readily soluble in water and readily so in alcohol or chloroform. It is sparingly soluble in ethyl acetate and practically insoluble in ether.

A sample dried at 100° examined in aqueous solution in a 200 mm. tube gave the following result: 0·6176 gram in 25 c.c. of solution gave a 0·73°, $[a]_D$ 14·8°, $[M]_D$ 56·1°. Taking the molecular rotation of the acid ion as 49°, that of the base is $[M]_D$ 7°.

UNIVERSITY COLLEGE,
    NOTTINGHAM.   [*Received, December* 16*th,* 1918.]

VI.—*Chromatocobaltiammines.*

By SAMUEL HENRY CLIFFORD BRIGGS.

PREVIOUS investigations have shown that the chromate radicle possesses considerable residual affinity, and has a strongly marked tendency to form complex salts (Briggs, *Zeitsch. anorg. Chem.,* 1907, **56**, 246; 1909, **63**, 325; Groeger, *ibid.,* 1908, **58**, 412). It was therefore to be expected that the chromatocobaltiammines would be a well-defined and stable class of substances, containing one or more non-ionisable chromate radicles. As soluble compounds containing a non-ionisable chromate radicle have not previously been described, the study of the chromatocobaltiammines was undertaken in order to compare the properties of the chromate radicle in non-ionisable combination with those of the ionisable radicle in the ordinary chromates.

The chromatocobaltiammines are readily prepared by the action of potassium chromate on the corresponding aquo-compounds in solution. Thus, when a solution of potassium chromate is added to a warm solution of an aquopentamminecobaltic salt, a chromato-

pentamminecobaltic salt (I)·crystallises out on cooling. The *nitrate*, *chloride*, and *chromate* of this series were obtained in a pure condition.

The chromatotetramminecobaltic salts (II) are formed in a similar manner, and the *chromate, dichromate,* and *nitrate* were prepared in a pure state. When a solution of a diaquotetramminecobaltic salt is treated with an excess of potassium chromate, *trichromato-octamminedicobalt* (III) crystallises out on keeping. Trichromato-octamminedicobalt is isomeric with chromatotetramminecobaltic chromate (IV), but the two compounds are very different. The former is almost completely insoluble in water, and forms greenish-black crystals containing five molecules of water of crystallisation, whilst the latter is obtained as a greenish-brown precipitate with three molecules of water of crystallisation; it is moderately soluble in water, and its solution gives the reactions of the chromate ion.

.Attempts to prepare chromatotriammine compounds by the action of potassium chromate on triaquotriamminecobaltic nitrate were not successful, the product being chromatohydroxotriamminecobalt (V), which, however, was not obtained in a completely pure condition. It therefore appears that when more than two molecules of ammonia in the hexamminecobaltic radicle are replaced by the chromate radicle, the products are unstable in the presence of water, and undergo hydrolysis. This explains why endeavours to prepare potassium cobaltic chromate, $K_3Co(CrO_4)_3$, by oxidising cobaltous salts in the presence of potassium chromate, failed, cobaltic hydroxide and potassium dichromate being obtained. The formation of chromatohydroxotriamminecobalt in the above manner also supports the view that the basic chromates are hydroxo-compounds in accordance with Werner's theory of basic salts ("Neuere Anschauungen auf dem Gebiete der anorganischen Chemie," 3rd ed., pp. 177–178).

Some evidence was obtained which pointed to the existence of a chromatoaquotriammine series (VI), a compound being prepared which had the composition of chromatoaquotriamminecobaltic dichromate:

$$\left(Co\begin{smallmatrix}5NH_3\\CrO_4\end{smallmatrix}\right)X \qquad Co\begin{smallmatrix}4NH_3\\CrO_4\end{smallmatrix}\dot{)}X \qquad \left(Co\begin{smallmatrix}4NH_3\\CrO_4\end{smallmatrix}CrO_4\begin{smallmatrix}4NH_3\\CrO_4\end{smallmatrix}Co\right)$$

$$\text{(I.)} \qquad\qquad \text{(II.)} \qquad\qquad \text{(III.)}$$

$$\left(Co\begin{smallmatrix}4NH_3\\CrO_4\end{smallmatrix}\right)_2 CrO_4 \qquad Co\begin{smallmatrix}CrO_4\\OH\\3NH_3\end{smallmatrix} \qquad Co\begin{smallmatrix}CrO_4\\H_2O\\3NH_3\end{smallmatrix}X$$

$$\text{(IV.)} \qquad\qquad \text{(V.)} \qquad\qquad \text{(VI.)}$$
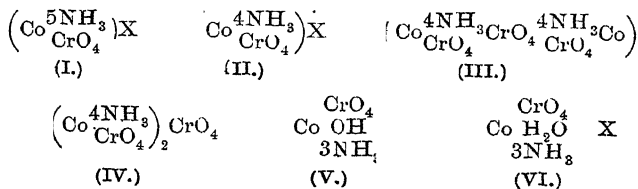
In the chromatopentammine- and chromatotetrammine-cobaltic salts the chromate radicle in the complex is non-ionisable, no pre-

cipitate being obtained when silver nitrate is added to cold, freshly prepared solutions of the pure nitrates. If the mixture is allowed to remain for some time, however, silver chromate is slowly deposited, showing that the chromato-salts have a tendency to pass into the corresponding aquo-salts as seen from the equation :

$$\left(\mathrm{Co}_{5\,N\,H_3}^{\mathrm{CrO_4}}\right)\mathrm{NO_3} + 2\mathrm{AgNO_3} + \mathrm{H_2O} = \left(\mathrm{Co}_{5\,N\,H_3}^{\mathrm{H_2O}}\right)(\mathrm{NO_3})_3 + \mathrm{Ag_2CrO_4}.$$
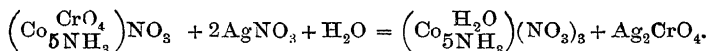
If the solution is heated the change takes place at once, and silver chromate is immediately precipitated.

The chromate radicle in these compounds reacts with hydrogen ions in the same way as in the ordinary chromates. When an acid is added to a solution of a chromatopentammine or chromato-tetrammine salt, the complex is decomposed, as seen from the change in colour of the solution.

In the chromatopentammine salts the chromate radicle fills one co-ordination position according to Werner's theory, whereas in the chromatotetrammine salts it fills two positions.

The entrance of the chromate radicle into the complex is accompanied by marked intensification of colour, and all the chromato-cobaltiammines are deeply coloured substances.

<div align="center">Experimental.</div>

<div align="center">*Pentammine Series.*</div>

Chromatopentamminecobaltic Nitrate, $\left(\mathrm{Co}_{\mathrm{CrO_4}}^{5\,N\,H_3}\right)\mathrm{NO_3}$.—Carbon-atopentamminecobaltic nitrate was converted into aquopentammine-cobaltic nitrate, and potassium chromate was then added to the solution, the details of the preparation being as follows.

Carbonatopentamminecobaltic nitrate (2·5 grams) was dissolved in 100 c.c. of water, a little dilute nitric acid was added, and the solution was gently warmed to expel carbon dioxide. The liquid was then just neutralised by potassium hydroxide, diluted to 300 c.c., and heated to 60—70°. One and a-half grams of potassium chromate in 100 c.c. of water also heated to 60—70° were added, and the clear solution was allowed to crystallise. The chromatopentamminecobaltic nitrate separated in brownish-red, acicular crystals (2·2 grams), which were collected, washed with a little water, and dried in the air.

Found : Co = 18·51 ; CrO$_3$ = 31·74 ; NH$_3$ = 26·36.

$\left(\mathrm{Co}_{\mathrm{CrO_4}}^{5\,N\,H_3}\right)\mathrm{NO_3}$ requires Co = 18·35 ; CrO$_3$ = 31·05 ; NH$_3$ = 26·44 per cent.

The salt was moderately soluble in cold water, and the freshly

prepared solution was not precipitated by silver, lead, or barium salts, but precipitation took place at once on heating. The chromate radicle is therefore situated in the complex, as shown by the above formula, and the salt is isomeric with Jörgensen's nitratopent-amminecobaltic chromate, $\left(\mathrm{Co}_{\mathrm{NO_3}}^{5\mathrm{NH_3}}\right)\mathrm{CrO_4}$ (*J. pr. Chem.*, 1881, [ii], **23**, 245).

Chromatopentamminecobaltic Chloride, $\mathrm{Co}_{5\mathrm{NH_3}}^{\mathrm{CrO_4}}\Big)\mathrm{Cl}$.--Chloro-pentamminecobaltic chloride was converted into aquopentamminecobaltic chloride by Werner's method (*Ber.*, 1907, **40**, 4104), and this was treated with potassium chromate.

Twenty-five grams of chloropentamminecobaltic chloride were heated with 625 c.c. of water and 62·5 c.c. of concentrated aqueous ammonia until the chloride was completely dissolved. After cooling, the liquid was just neutralised with hydrochloric acid, and heated to 60°. Sixteen grams of potassium chromate in 500 c.c. of water, also heated to 60°, were then added, and the mixture was allowed to cool. After crystallisation was complete, the salt was collected, washed with a little water, and dried in the air. Twenty-three grams of brownish-red crystals (*A*) were thus obtained. The mother liquor was heated to 50° and 4 grams of potassium chromate dissolved in a little water were added. On cooling, 1·2 grams of a second salt (*B*) were obtained in yellowish-brown prisms, almost insoluble in cold water, but readily soluble on warming to give a yellow solution. The salt *A* was anhydrous, but *B* contained water of crystallisation; otherwise the salts were similar in composition, as seen from the analyses :

A. Found : $\mathrm{Co}=19\cdot86$; $\mathrm{CrO_3}=33\cdot97$, $34\cdot27$; $\mathrm{Cl}=12\cdot02$; $\mathrm{NH_3}=27\cdot30$, $27\cdot15$, $27\cdot08$.

$\left(\mathrm{Co}_{5\mathrm{NH_3}}^{\mathrm{CrO_4}}\right)\mathrm{Cl}$ requires $\mathrm{Co}=19\cdot96$; $\mathrm{CrO_3}=33\cdot83$; $\mathrm{Cl}=12\cdot00$; $\mathrm{NH_3}=28\cdot81$ per cent.

B. Found : $\mathrm{Co}=16\cdot91$; $\mathrm{Cl}=9\cdot80$; $\mathrm{CrO_3}=29\cdot94$; $\mathrm{NH_3}=26\cdot6$; $\mathrm{H_2O}=13\cdot95$.

$2\left(\mathrm{Co}_{5\mathrm{NH_3}}^{\mathrm{Cl}}\right)\mathrm{CrO_4}{,}5\mathrm{H_2O}$ requires $\mathrm{Co}=17\cdot31$; $\mathrm{Cl}=10\cdot41$; $\mathrm{CrO_3}=29\cdot36$; $\mathrm{NH_3}=25\cdot0$; $\mathrm{H_2O}=13\cdot22$ per cent.

The solution of the salt *A* on addition of silver nitrate gave a copious precipitate. This was filtered off, and on treatment with dilute nitric acid was found to consist of silver chloride coloured by the presence of a trace of silver chromate. The reddish-yellow filtrate, on heating, deposited a precipitate of silver chromate. The

salt A was therefore *chromatopentamminecobaltic chloride*, $Co \overset{CrO_4}{\underset{5NH_3}{}} Cl$.

The solution of the salt B on addition of silver nitrate gave a red precipitate, which was filtered off, the filtrate being only faintly coloured. The precipitate consisted of silver chromate. It dissolved in dilute nitric acid, leaving only a trace of silver chloride. The salt B was therefore a hydrated *chloropentamminecobaltic chromate*, $2\left(Co \overset{Cl}{\underset{5NH_3}{}}\right)CrO_4, 5H_2O$.

Various preparations of the salt A (chromatopentamminecobaltic chloride) were made, but in all cases the ammonia content was low. The salt could not be purified by crystallisation from hot water, as it was then found to contain a little of the corresponding chromate, $\left(Co \overset{CrO_4}{\underset{5NH_3}{}}\right)_2 CrO_4$, which is very sparingly soluble in water. The reason for the low percentage of ammonia could not be ascertained, and this is all the more remarkable as the salt, on treatment with silver chromate, gave the corresponding chromate in a high degree of purity.

Chromatopentamminecobaltic Chromate, $\left(Co \overset{CrO_4}{\underset{5NH_3}{}}\right)_2 CrO_4, 3H_2O$. —Two grams of silver nitrate were precipitated in the cold with 1 gram of potassium chromate, and the precipitate was washed two or three times by decantation. The supernatant liquid was separated as far as possible by decantation, and the precipitate was then poured into a solution of 3 grams of chromatopentamminecobaltic chloride in 150 c.c. of water at 60°, the mixture being well shaken. After a few minutes the silver chloride assumed a dense form, and crystallisation began. The silver chloride was then rapidly collected, and the filtrate, which no longer gave the reactions of the chloride ion, was allowed to crystallise. *Chromatopentamminecobaltic chromate* separated in glistening, scaly crystals, similar in colour to silver chromate. The yield was 1·5 grams. The crystals consisted of a trihydrate, which lost $2\frac{3}{4}$ molecules of water after exposure over sulphuric acid in a vacuum for two or three weeks (loss = 7·16. $2\frac{3}{4}H_2O$ require a loss of 7·17 per cent.). The resulting hydrate, $4\left(Co \overset{CrO_4}{\underset{5NH_3}{}} CrO_4, H_2O\right)_2$, became anhydrous above 100°. The complete analysis of the trihydrate gave:

Found : Co = 17·48 ; CrO_3 = 43·64 ; NH_3 = 24·83 ; H_2O = 7·64.

$\left(Co \overset{CrO_4}{\underset{5NH_3}{}}\right)_2 CrO_4, 3H_2O$ requires Co = 17·09 ; CrO_3 = 43·6 ; NH_3 = 24·68 ; H_2O = 7·83 per cent.

Tetrammine Series.

Carbonatotetramminecobaltic nitrate was prepared by Jörgensen's method (*Zeitsch. anorg. Chem.*, 1892, **2**, 282), and this was converted into diaquotetramminecobaltic nitrate by acidification of its solution. On treating the solution of diaquotetramminecobaltic nitrate with potassium chromate, either chromatotetramminecobaltic nitrate, chromatotetramminecobaltic chromate, or trichromato-octamminedicobalt could be obtained in the pure state, according to the conditions employed.

Chromatotetramminecobaltic Nitrate, $2\left(Co\frac{CrO_4}{4NH}\right)NO_3,H_2O$.—A solution of 4 grams of carbonatotetramminecobaltic nitrate in a little water was treated with dilute nitric acid, warmed gently to expel carbon dioxide, just neutralised with potassium hydroxide, and the volume made up to 40 c.c. Twenty grams of ammonium nitrate were dissolved in the liquid, and a solution of 1·2 grams of potassium chromate in 10 c.c. of water was added, drop by drop, in the cold, with vigorous stirring. The stirring was continued for a minute or two until crystallisation was complete, and the dark reddish-brown deposit was then immediately collected, washed with a little water, and dried in the air. The yield was 0·9 gram. The product was a hemihydrate, which lost its water of crystallisation after exposure for two days over sulphuric acid in a vacuum.

Found : $Co = 18\cdot86$; $CrO_3 = 31\cdot68$; $NH_3 = 21\cdot34$; $H_2O = 3\cdot67$.

$2\left(Co\frac{CrO_4}{4NH_3}\right)NO_3,H_2O$ requires $Co = 18\cdot77$; $CrO_3 = 31\cdot83$; $NH_3 = 21\cdot69$

$H_2O = 2\cdot87$ per cent.

The salt was moderately soluble in water, giving a deep brown solution. Silver, barium, or lead salts did not precipitate the freshly prepared, cold solution, but precipitation took place at once on heating. The cold solution was also completely precipitated if allowed to remain for several days after the addition of the reagent, showing that the chromate radicle is gradually eliminated with the formation of a diaquotetrammine salt, for example,

$$\left(Co\frac{CrO_4}{4NH_3}\right)NO_3 + 2AgNO_3 + 2H_2O = \left(Co\frac{2H_2O}{4NH_3}\right)(NO_3)_3 + Ag_2CrO_4.$$
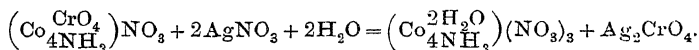
Chromatotetramminecobaltic Chromate, $\left(Co\frac{CrO_4}{4NH_3}\right)_2 CrO_4,3H_2O$.— Four grams of carbonatotetramminecobaltic nitrate in 80 c.c. of water were converted into diaquotetramminecobaltic nitrate as described above in the preparation of chromatotetramminecobaltic nitrate. To the cold neutral solution of diaquotetramminecobaltic

nitrate thus obtained (100 c.c.) 3 grams of potassium chromate, dissolved in 50 c.c. of water, were added with vigorous stirring. A brown, crystalline precipitate was formed, which was collected immediately, washed with water, and dried with alcohol and ether. The yield was 2·8 grams.

The salt contained three molecules of water as water of crystallisation only, being readily evolved when the substance was exposed in a vacuum over sulphuric acid. The salt was sparingly soluble in water, and its solution was immediately precipitated by silver nitrate, showing that some of the chromate content was ionisable. It follows from these facts and the analyses that the compound must have the formula assigned to it.

Found : Co = 18·14 ; CrO_3 = 45·31 ; NH_3 = 20·61 ; H_2O = 8·26.

$\left(Co\dfrac{CrO_4}{4NH_3}\right)_2 CrO_4, 3H_2O$;   Co = 17·97 ; CrO_3 = 45·71 ; NH_3 = 20·77 ; H_2O = 8·26 per cent.

Trichromato-octamminedicobalt,

$$\left(Co\dfrac{CrO_4}{4NH_3}-CrO_4-\dfrac{Cr O_4}{4NH_3}Co\right), 5H_2O.$$
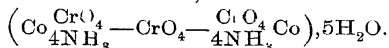
—Two grams of carbonatotetramminecobaltic nitrate in 30 c.c. of water were converted into diaquotetramminecobaltic nitrate in the manner already described, and the cold neutral solution (50 c.c.) was added, with stirring, to a cold solution of 5 grams of potassium chromate in 50 c.c. of water. The clear liquid deposited a greenish-black, crystalline substance on keeping. This was collected, washed with a little water, and dried in the air.

Found : Co = 17·14 ; CrO_3 = 43·32 ; NH_3 = 19·44 ; H_2O = 13·05.

$Co_2 8NH_3 (CrO_4)_3, 5H_2O$ requires Co = 17·04 ; CrO_3 = 43·33 ; NH_3 = 19·68 ; H_2O = 13·01 per cent.

The five molecules of water were readily evolved on exposing the compound in a vacuum over sulphuric acid, and all were therefore water of crystallisation only. In view of the facts ascertained with regard to chromatotetramminecobaltic chromate and described above, it follows that this isomeric compound must be a non-ionisable octamminedicobalt derivative. Its almost complete insolubility in water affords further confirmation of this view. Again, since in the diaquotetramminecobaltic salts the water molecules are in the " *cis* " position (Werner, " Neuere Auschauungen auf dem Gebiete der anorganischen Chemie," 3rd ed., p. 347), this trichromato-octamminedicobalt must also have the chromate radicles in the " *cis* " position, and is therefore a 1 : 1′ : 2-2′-*trichromato-octamminedicobalt pentahydrate.* Attempts to prepare the corresponding " *trans* " compound by various methods were unsuccessful.

Chromatotetramminecobaltic Dichromate, $\left(Co\dfrac{CrO_4}{4NH_3}\right)_4$ $Cr_2O_7,2H_2O$.
—Four grams of carbonatotetramminecobaltic nitrate were converted into diaquotetramminecobaltic nitrate as described above, and the neutral solution (80 c.c.) was added slowly, with stirring, to a cold solution of 8 grams of potassium dichromate in 80 c.c. of water. The precipitate was immediately collected, washed with a little water, and dried in the air. The yield was 1·9 grams. Three separate preparations were analysed, and the ammonia content was low in every case, for some reason that could not be ascertained.

Found: Co = 15·94; CrO_3 = 53·41, 54·01; NH_3 = 17·48, 16·6, 16·4; H_2O = 4·98, 4·76, 5·04.

$\left(Co\dfrac{CrO_4}{4NH_3}\right)_2 Cr_2O_7,2H_2O$ requires Co = 15·97; CrO_3 = 54·19; NH_3 = 18·4; H_2O = 4·88 per cent.

The three molecules of water were readily given off in a vacuum over sulphuric acid, and all were therefore water of crystallisation only. From the proportion of cobalt to chromium (2Co : 4Cr) it is evident that the salt is chromatotetramminecobaltic dichromate, $\left(Co\dfrac{CrO_4}{4NH_3}\right)_2 Cr_2O_7$, and not dichromatotetramminecobaltic chromate, $\left(Co\dfrac{Cr_2O_7}{4NH_3}\right)_2 CrO_4$, in which the proportions are 2Co : 5Cr. Consequently the dichromate radicle is ionisable, and the chromate radicle non-ionisable. The salt was moderately soluble in water, and the solution was immediately precipitated by silver and barium salts.

Triammine Series.

Chromatohydroxotriamminecobalt.—Two grams of trinitratotriamminecobalt prepared by Jörgensen's method (*Zeitsch. anorg. Chem.*, 1895, **5**, 185) were dissolved in 40 c.c. of cold water, and the solution was added to a cold solution of 6 grams of potassium chromate in 40 c.c. of water. The brown precipitate (1) was collected, washed with cold water, and dried in the air, when it weighed 1·7 grams. The filtrate, on spontaneous evaporation, deposited crystals of potassium dichromate, as well as of potassium chromate. Two other preparations were made (2 and 3), in which 1 gram of potassium chromate in 10 c.c. of water was mixed with 6·25 c.c. of potassium hydroxide solution (1 c.c. = 0·0448 gram KOH), and the mixture was poured into a solution of 1·5 grams of trinitratotriamminecobalt in 10 c.c. of cold water. The analyses gave:

Found: (1) $H_2O = 11.5$; $CrO_3 = 36.3$; $Co = 22.9$; $NH_3 = 15.1$.
       (2) $H_2O = 11.4$; $CrO_3 = 34.5$; $Co = 22.5$; $NH_3 = 16.8$.
       (3) $NH_3 = 16.7$.

$\left(\begin{matrix} OH \\ CoCrO_4 \\ 3NH_3 \end{matrix} \right), 2H_2O$ requires $H_2O = 12.9$ $CrO_3 = 35.8$; $Co = 21.1$;
     $NH_3 = 18.3$ per cent.

Although impure, the compound was clearly a hydrated chromato-hydroxotriamminecobalt.

Chromatoaquotriamminecobaltic Dichromate.—Two grams of trinitratotriamminecobalt in 10 c.c. of cold water were added to a solution of 3 grams of sodium dichromate in 10 c.c. of water, and the mixture was treated with a solution of 0.75 gram of anhydrous sodium chromate in 10 c.c. of water, in the cold. A copious brown precipitate was formed, which was allowed to settle, and then collected, washed with a little water, and dried with alcohol and ether. The product, which weighed 1.4 grams, was only sparingly soluble in cold water. In a vacuum over sulphuric acid, it lost 3 molecules of water after three days, and a further quarter molecule after eighteen days, the weight then remaining constant. The analysis agreed closely with the formula given below.

Found: $3H_2O = 7.22$; $3\tfrac{1}{4}H_2O = 8.16$; $Co = 16.06$; $CrO_3 = 54.09$;
     $NH_3 = 13.63$.

$\left(\begin{matrix} H_2O \\ CoCrO_4 \\ 3NH_3 \end{matrix} \right)_2 Cr_2O_7, 2H_2O$ requires $3H_2O = 7.30$; $3\tfrac{1}{4}H_2O = 7.91$; $Co = $
     15.93; $CrO_3 = 54.04$; $NH_3 = 13.81$ per cent.

Note on the Preparation of Carbonatopentamminecobaltic Nitrate.

The following method of preparation was found to be more convenient and more economical than that described by Werner and Goslings (*Ber.*, 1903, **36**, 2380).

Twenty grams of cobalt carbonate were dissolved in the smallest possible quantity of dilute nitric acid and the clear solution (100 c.c.) was poured into a mixture of 250 c.c. of concentrated aqueous ammonia and 100 grams of powdered ammonium carbonate. Air was drawn through for two or three hours and the solution was then allowed to remain for twenty-four hours. The mixture was heated for twenty minutes in a porcelain dish on the water-bath with frequent addition of a small piece of ammonium carbonate. The brown colour of the liquid changed to deep red, and the mixture was allowed to remain until crystallisation was complete. After filtration and washing with a little water, the salt

was digested with cold water to remove any ammonium carbonate still present. The air-dried product weighed 21 grams. (Found, $Co = 20·54$; $NH_3 = 29·63$. $\left(Co\dfrac{5NH_3}{CO_3}\right)NO_3, H_2O$ requires $Co = 20·76$; $NH_3 = 29·95$ per cent.) The water was not given off at $100°$, or in a vacuum over sulphuric acid at the ordinary temperature.

VII.—*Glyceryl Methyl Ether Dinitrate (a-Methylin Dinitrate.)*

By DAVID TREVOR JONES.

DURING recent years, considerable attention has been devoted to the study of the mono- and di-nitrates of glycerol and their chlorides and ethers. The interest in these substances has been stimulated by the technical possibilities which they appeared to offer as ingredients of non-freezing nitroglycerin blasting compositions. Among the substances investigated have been the dinitrate of monochlorohydrin (Kast, *Zeitsch. ges. Schiess- u. Sprengstoffw.*, 1906, **1**, 227), which has been more or less extensively used in such explosives as gelatin astralit, gelatin westfalit, etc. The mono- and di-nitrates of glycerol have been very exhaustively studied by Will (*Ber.*, 1908, **41**, 1107), who commenced the investigation of these substances with the above-mentioned technical object in view. The dimethyl and diethyl ethers of glycerol mononitrate have been described by Paternò and Benelli (*Gazzetta*, 1909, **39**, ii, 312), whilst Vender has described the dinitrates of monoacetin and monoformin (*Zeitsch. ges. Schiess- u. Sprengstoffw.*, 1907, **2**, 21).

Glyceryl methyl ether dinitrate, which is here described, was prepared by the direct nitration of the α-monomethyl ether of Grün and Bockisch (*Ber.*, 1908, **41**, 3471).

$$OMe·CH_2·CH(OH)·CH_2·OH + 2HNO_3 \longrightarrow$$
$$OMe·CH_2·CH(NO_3)·CH_2·NO_3 + 2H_2O.$$
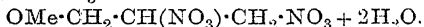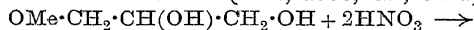
The product, which was readily isolated, was found to solidify after being well supercooled and stirred. It is a powerful explosive, having about two-thirds the strength of nitroglycerin. It is, however, much less sensitive to shock, although rather more readily exploded by heat. Its effect in lowering the freezing point of nitroglycerin is much the same as that of molecular concentra-

tions of monochlorohydrin dinitrate (Kast, *loc. cit.*) and of ethyl nitrate (Nauckhoff, *Zeitsch. angew. Chem.*, 1905, **18**, 21). All these values, however, are in complete disagreement with the value for the freezing-point constant of nitroglycerin as calculated from a carefully conducted determination of its latent heat of fusion (Hibbert and Fuller, *J. Amer. Chem. Soc.*, 1913, **35**, 979).

The substance did not appear to exist in a second or labile form corresponding with the labile form of nitroglycerin.

Experimental.

Glyceryl α-monomethyl ether was prepared by Grün and Bockisch's method (*loc. cit.*). The product distilled at 120°/18 mm., and the yield was 127 grams, or from 200 grams of monochlorohydrin 66 per cent. of the theoretical. The same yield was obtained on repeating the experiment.

Glyceryl Methyl Ether Dinitrate.

Sixty-three grams of glyceryl α-monomethyl ether were gradually added to 480 grams of a mixture of nitric and sulphuric acids ($HNO_3 = 38·6$, $H_2SO_4 = 59·0$, $H_2O = 2·4$ per cent.), which was cooled in ice-water during the nitration. The initial temperature was 13°. During the operation, the temperature was allowed to rise to 20°, and was maintained at that point until the end. The nitration proceeded quite smoothly, and was easily controlled by regulating the addition of the glyceryl methyl ether. The time occupied by the nitration was from twenty to twenty-five minutes. The product was completely soluble in the mixed acid, and the mixture was slowly poured into 800 c.c. of water, the temperature being allowed to rise to 40°. The bulk of the dinitrate separated, and, after remaining for some little time, the bulk of the aqueous layer was poured off and preserved for extraction. The residue containing the dinitrate was neutralised with a semi-saturated solution of sodium carbonate. The dinitrate was then run off from below, the neutralised aqueous layer being added to the diluted acid which had been previously poured off. The dinitrate was then washed three times at 50° with an equal bulk of 5 per cent. sodium carbonate solution, then three times with water, and was finally dried in a desiccator over calcium chloride. The yield was 75 grams, or 64 per cent. of the theoretical. The neutralised aqueous washings were extracted with ether, and the ethereal solution was washed with 5 per cent. sodium carbonate solution, dried with calcium chloride, filtered, evaporated under diminished

pressure, and preserved over calcium chloride in a desiccator. In this way, a further yield of 13·9 grams was obtained, the total yield being thus 88·9 grams, or 77 per cent. of the theoretical.

The dry liquid constituting the first and major portion of the yield was analysed by the combustion method, but on account of its highly explosive nature the weighed-out substance was first converted into a weak dynamite by mixing with excess of previously ignited kieselguhr, the dynamite in turn being mixed with roughly powdered copper oxide and introduced into the combustion tube. The combustion proceeded normally.

The nitrogen was estimated by the nitrometer method, using sulphuric acid, as in the analysis of guncotton:

0·1397 gave 0·1248 CO_2 and 0·0514 H_2O.   C = 24·36; H = 4·03.
0·5492   ,,   132·3 c.c. NO at 16° and 755 mm.   N = 14·15.
0·638 in 20·45 benzene gave $\Delta^t = -0·833°$.   M.W. = 188.
  $C_4H_8O_7N_2$ requires C = 24·28; H = 4·08; N = 14·29 per cent.
                    M.W. = 196.

The substance was therefore undoubtedly α-methylin dinitrate.

Glyceryl methyl ether dinitrate crystallises in white, monoclinic prisms melting at 24°. As first obtained, it was a clear, colourless liquid, which became pale yellow on keeping. It crystallised with difficulty, and remained liquid, even with occasional shaking, for more than two years in a magazine maintained at 15—21°. It distilled at 124°/18 mm., that is, at approximately the same temperature as the glyceryl methyl ether from which it was derived, and some 22° lower than glyceryl dinitrate, the corresponding alcohol.

It is therefore more volatile than nitroglycerin, and when tested at 100° on a watch-glass it was found to volatilise at from seven to eight times as rapidly. The liquid has D_{15}^{15} 1·374 and n_D^{21} 1·4478. It is soluble in benzene, toluene, acetic acid, methyl and ethyl alcohols, chloroform, ether, or acetone, and insoluble in carbon disulphide or light petroleum.

It gelatinises nitro-cotton rapidly at the ordinary temperature, and after warming it yields a gelatin softer and more plastic than that obtained from nitroglycerin.

The chief interest of this substance lies in its explosive properties as compared with those of nitroglycerin. It has about two-thirds the power of nitroglycerin, although it is much less sensitive to shock. Its comparative insensitiveness was demonstrated by submitting to the fall-hammer test unfrozen dynamites each containing three parts of explosive to one part of kieselguhr. Both substances were placed under a steel disk and subjected to the

impact of a weight of 1 kilogram, falling from a measured height.
The results are set forth in the following table:

Dinitrate.			Nitroglycerin.		
Height of fall. cm.	Detonations.	Failures.	Height of fall. cm.	Detonations.	Failures.
100	2	8	30	10	0
95	1	9	20	10	0
90	1	9	15	9	1
85	0	10	10	0	10

The solid substance was very insensitive. It did not explode
even when scratched with the sharp edge of a thin melting-point
tube. On the other hand, the dinitrate proved to be more easily
exploded when heated than did nitroglycerin. When heated in a
glass test-tube in a metal-bath, the temperature being raised at the
rate of 5° per minute, it was observed to explode at 182°, the tri-
nitrate exploding at 192°.

Comparative power tests of nitroglycerin and methylin dinitrate
dynamites were made with the Trauzl lead block and mortar tests.
In the lead block, the dinitrate dynamite gave an expansion of
22·9 c.c., a similar charge of nitroglycerin dynamite giving 30·0 c.c.
In the mortar test, the relative powers indicated by the ballistic
pendulum were 93·76 kilogram-metres (678 foot-lb.) for the
dinitrate dynamite as compared with 124·43 kilogram-metres
(900 foot-lb.) for a similar charge of nitroglycerin dynamite.
Methylin dinitrate, therefore, would appear to have rather more
than two-thirds the strength of nitroglycerin.

In order to determine the lowering effect of the dinitrate on
the freezing point of nitroglycerin, a form of apparatus was
adopted similar to that used by Kast (*loc. cit.*) for determining
the melting points of the nitroglycerin isomerides, and by Hibbert
(*Eighth International Congress of Applied Chemistry*, 1912,
IV, 37).

About 5 c.c. of the mixture were inserted in a test-tube
(15 × 1 cm.) which was fitted into a slightly larger tube, whereby
the glyceryl nitrates were protected by an air-jacket from the too
rapid action of the freezing mixture. The freezing agent con-
sisted of ice where mixtures of higher melting point were con-
cerned, and of ice and salt for those of lower melting point. The
thermometer was allowed to stand in the mixture, direct contact
between glass and glass being prevented by enclosing the lower
portion of the thermometer bulb in a band of elastic. The stirrer
consisted of a flexible piece of platinum wire which was attached
to a weighted string wound over a simple pulley, and fastened at

the further end to the outer edge of a wooden disk rotated by a motor. The liquid was first supercooled to the extent of about 4° or 5°. It was then inoculated with a small quantity of a frozen mixture of nitroglycerin, wood-pulp, and sodium nitrate, and vigorously stirred. The maximum temperature was then carefully noted and taken as the freezing point. It will be seen that the values found for the molecular depression constant for nitroglycerin vary from 72·4 to 81·0, thus differing not very greatly from those obtained by Nauckhoff (*loc. cit.*) and by Kast (*loc. cit.*) with ethyl nitrate and monochlorohydrin dinitrate respectively. These numbers are in fair agreement with the value 70·5 for the freezing-point constant for nitroglycerin obtained by Nauckhoff (*loc. cit.*) from a determination of its latent heat of fusion. Nauckhoff's method was, however, admittedly defective, and his results differ very considerably from those of Hibbert and Fuller (*loc. cit.*), who found the latent heat of fusion (h) of nitroglycerin at 0° to be 33·2 calories. Corrected to 13°, the melting point of stable nitroglycerin, this would become $33·2 + 13·0 \ (c_1 - c_2)$, where c_1 and c_2 are the specific heats of solid and liquid nitroglycerin respectively. Accepting Nauckhoff's values of 0·356 and 0·315 for these, the latent heat of fusion of nitroglycerin at 13° would be $33·2 + 13·0 \ (0·356 - 0·315) = 34·33$.

Hence the freezing-point constant

$$\frac{RT^2}{100h} \ = \ \frac{0·1991 \times (273 + 13)^2}{100 \times 34·33} \ = \ 48·5.$$

The results are set forth in the following table, which includes Nauckhoff's and Kast's values derived from ethyl nitrate and chlorohydrin dinitrate:

Composition of liquid.		Depression of freezing point. (Δ)	Molecular depression constant.	
Nitroglycerin. Grams.	Methylin dinitrate. Grams.		Calculated from Δ	Calculated from latent heat (Hibbert and Fuller).
31·69	1·802	2·1°	72·4	48·5
15·31	1·748	4·4	75·6	,,
8·22	1·729	8·7	81·0	,,
	Chlorohydrin dinitrate.			
21	2·1	4·4	88·4	,,
21	4·2	6·4—7·2	62·7—70·5	
21	6·3	9·4	60·7	
	Ethyl nitrate.		74·1	
			76·0	

Attempts to obtain a labile form of the substance analogous to that of nitroglycerin were made.   The liquid was mixed with glass wool and supercooled to varying degrees, with continual stirring with a glass rod.   When some of the supercooled liquid which had not been previously frozen was inoculated with a trace of this product, the solid obtained invariably crystallised at 24°.

The author desires to express his indebtedness to Messrs. Nobel's Explosive Co. and to Mr. W. Rintoul, the manager of their Research Section, for the facilities accorded to him for the carrying out and publication of this work.

VIII.—*The Inflammation of Mixtures of Ethane and Air in a Closed Vessel : The Effects of Turbulence.*

By RICHARD VERNON WHEELER.

WHEN describing the inflammation of mixtures of methane and air it was noted that the speed at which flame spreads through the mixture in a closed vessel is demonstrably dependent on the degree of mechanical agitation imparted to the mixture, as, indeed, is the speed of flame in all combustible mixtures and under all conditions other than those existing during the propagation of the explosion wave.

This important fact appears first to have been observed, or, at all events, first commented on by Schloësing and de Mondésir about the year 1864.   Their experiments, which involved an extended study of the mode of propagation of flame, were carried out mainly with mixtures of carbon monoxide and air, and were undertaken in connexion with a research on the working of gas engines.   Mallard and Le Chatelier, to whom the results of the experiments were communicated verbally, have thus described them (*Ann. des Mines*, 1883, [VIII], **4**, 298) :

"Ces recherches ont mis en évidence un fait d'une grande importance, l'influence de l'agitation du mélange gazeux sur la vitesse de propagation de la flamme.   Des mélanges très lents (et par cette expression nous entendrons ceux dans lesquels la vitesse de propagation est faible) peuvent donner lieu à des propagations pour ainsi dire instantanées, c'est-à-dire à de véritables explosions, quand on provoque au moment de l'inflammation une agitation intérieure très

vive, telle que celle que l'on obtient en faisant déboucher au milieu d'une masse gazeuse en repos un jet de gaz animé d'une grande vitesse."

These observations appear to have been overlooked or forgotten until the subject of the agitation or turbulence of gaseous mixtures became of manifest importance during the investigation of gaseous explosions instituted by the British Association for the Advancement of Science. New experiments on the subject, by Dugald Clerk and Hopkinson, are recorded in the Fifth Report of the Committee on Gaseous Explosions (*Rep. Brit. Assoc.*, 1912, 201).

To quote from his Gustave Canet lecture (Junior Institution of Engineers, 1913), Dugald Clerk "had long ago observed that gas engines would have been impracticable had the rates of explosion been the same in actual engine cylinders as in closed-vessel experiments." During his experiments in 1912 he "found that the rate of explosion rise in the same engine varied with the rate of revolution, increasing with increased number of rotations per minute, and was due to the turbulence or eddying caused by the rush of gases into the cylinder during the suction stroke, which persisted during the compression stroke."

By drawing in a charge of mixture into the gas-engine cylinder in the ordinary way, and then tripping the valves and compressing and expanding the charge for one or two revolutions before igniting it, the turbulence was given time to die away. It was found that the effect of thus damping down turbulence was to retard the rate of inflammation of the mixture to a remarkable extent. For example, with a mixture of coal-gas and air containing about 9·7 per cent. of gas, ignition in a gas-engine cylinder under normal conditions at the end of the first compression stroke (the engine being run at 180 revolutions per minute) resulted in the maximum pressure being attained after 0·037 sec. ; whilst when ignition was at the end of the third compression stroke, after the charge had been expanded twice and turbulence had subsided, the time taken for the attainment of maximum pressure was 0·092 sec.

Hopkinson experimented on the effects of turbulence at the same time as Dugald Clerk, using a cylindrical vessel 30·5 cm. in diameter and 30·5 cm. long. A small fan was mounted at the centre of the vessel, and comparison was made of the results of igniting similar mixtures with the fan at rest and in motion. With mixtures of coal-gas and air containing 10 per cent. of gas, the times that elapsed between ignition and the attainment of maximum pressure were: (1) with the fan at rest, 0·13 sec. ; (2) with the fan running at 2,000 revolutions per min., 0·03 sec. ; and (3) with the fan running at 4,500 revolutions per min., 0·02 sec.

Simultaneously with, and independently of, the experiments thus made on behalf of the Gaseous Explosions Committee of the British Association, a problem under investigation for the Explosions in Mines Committee of the Home Office was found to involve a study of the effects of turbulence on the inflammation of gaseous mixtures. The problem was to determine the effect, if any, of the presence of incombustible dusts in suspension on the limits of inflammability of mixtures of firedamp and air. A series of experiments on the ignition of mixtures near the lower limit of inflammability was made with a spherical vessel of about 4 litres capacity (described in T., 1918, **113**, 855) provided with a fan which could be rotated at a high speed so as to agitate the mixture and maintain dust in suspension. Naturally, the fan was rotated whether dust was present or absent, so as to ensure that the comparative experiments required should be made under as far as possible identical conditions. The pronounced effect of turbulence or agitation of a gaseous mixture on the speed at which flame travels through it thus became manifest, for many experiments had previously been made with similar mixtures in the same sphere without the fan.

The fan had four blades, and was attached to a horizontal shaft passing through an air-tight gland near the bottom of the sphere. Each blade extended for 7·5 cm. along the shaft and had a maximum width of 2·5 cm., the edge having a radius of curvature of 9·5 cm. The shaft was so fitted that there was a clearance of 1 cm. between the side of the sphere and the edges of the fan-blades. A slight helical twist was given to each blade.

Several experiments were made with mixtures of ethane and air near the lower-limit of inflammability, which, with ignition at the centre of a closed spherical vessel of glass of 2·5 litres capacity, is 3·10 per cent. ethane. With 3·0 per cent. of ethane flame travels slowly throughout nearly the whole of the (non-turbulent) mixture in such a vessel; and with 2·9 and 2·95 per cent. of ethane flame spreads through about one-third of the mixture (T., 1911, **99**, 2026). It will therefore be realised that even though a mixture may not contain sufficient ethane to ensure continued self-propagation of flame, part of the mixture may be burnt with a consequent development of pressure in a closed vessel.

The earlier experiments with turbulent mixtures were made with the fan running at 100 revolutions per second. The means of ignition was a secondary discharge (from a " 10-inch " X-ray coil) across a spark-gap of 12 mm. at the centre of the sphere, produced by breaking a current of 10 amperes in the primary circuit of the coil, the trembler being locked. Such a discharge is more than adequate to ignite any inflammable mixture of ethane and air when,

the mixture is still, yet it was found that no ignition, or, rather, no propagation of flame, took place with a mixture of ethane and air containing as much as 3·2 per cent. of ethane when that mixture was agitated by the fan at 100 revolutions per second. On stopping the fan and allowing the turbulence to subside, ignition took place readily with complete inflammation of the mixture and the development of a pressure of 3·4 atmospheres.

Similarly, with mixtures containing 3·15 and 3·05 per cent. of ethane no ignition could be obtained, whilst the fan was running (at 100 revolutions per second), however frequently the discharge was passed, although when the mixtures were free from turbulence ignition occurred on the first passage of the discharge. Details of these and similar experiments are as follow:

Ethane in mixture.
Per cent.   Result.
3·20   No ignition when the fan was running at 100 revolutions
              per sec. With the fan at 40 revolutions per sec. ignition
              took place, a pressure of 4·5 atm. being recorded 0·25
              sec. after ignition. Without the fan running, a pressure of
              3·4 atm. was developed.
3·15   No ignition could be obtained when the fan was run-
              ning at 100 revolutions per sec. Without the fan, ignition
              occurred at once, a pressure of 3·2 atm. being recorded.
3·10   With the fan at 40 revolutions per sec. ignition occurred
              on the fourth passage of the discharge. With the fan at
              20 revolutions per sec. ignition occurred at once. A
              pressure of 4·4 atm. was developed on both occasions,
              0·177 sec. after ignition in the first experiment, and
              0·287 sec. after ignition in the second.
3·05   No ignition could be obtained when the fan was run-
              ning at 100 revolutions per sec. Without the fan, ignition
              occurred at once and a pressure of 2·8 atm. was recorded.
3·00   No ignition with the fan at 100 revolutions per sec.
              With 20 revolutions per sec. ignition occurred at once
              and a pressure of 4·3 atm. was recorded 0·30 sec. after
              ignition.
2·95   With the fan running at 20 revolutions per sec. ignition
              occurred when the discharge was maintained (the
              trembler of the coil being in action). A pressure of 4·2
              atm. was recorded.

Strong agitation of a mixture poor in combustible gas renders it difficult to ignite, or, to be precise, renders it difficult for the flame that no doubt occurs during the passage of the discharge to spread away therefrom and travel throughout the mixture. This difficulty increases as the degree of agitation is increased and as the percentage of combustible gas is decreased. When, however, the flame in such an agitated mixture does manage to spread away from the source of ignition it travels rapidly.

From the high pressure developed when a mixture was ignited that contained 2·95 per cent. of ethane and to which turbulence

had been imparted by a fan running at 20 revolutions per second, it seemed that flame must have travelled through a greater proportion of the mixture than the one-third observed when the mixture was quiescent. An apparatus was therefore devised to enable the appearance of the flames in turbulent mixtures to be examined. The apparatus, which consisted essentially of a globe of glass of about 4 litres capacity, is shown in Fig. 1, and needs no description. Preliminary experiments were made to determine the direction of the air-currents induced by the fan, which had two helical blades and revolved on a vertical axis. From the behaviour of coloured powders introduced into the globe while the fan was spinning it appeared that air was drawn from the centre of the globe towards the axis of the fan, and was discharged at the periphery of the latter as a spiral current directed obliquely * around the walls of the globe.

Mixtures of methane and air were used for the experiments. Normally, the lower-limit for central ignition of methane–air mixtures in a closed sphere is 5·6 per cent. methane; the flame travels upward from the spark at the centre until it occupies one-third of the vessel, when it travels downwards as a horizontal disk to the bottom. The appearance of the flames in mixtures containing less than 5·6 per cent. of methane is shown in Fig. 3, T., 1911, **99**, 2025.

When a 5·6 per cent. mixture of methane and air was agitated by spinning the fan at about 50 revolutions per second, a succession of discharges from an induction coil, the trembler of which was in operation in the usual manner, apparently failed to cause ignition. On close observation, however, it was seen that a pointed tongue of flame appeared at each passage of the discharge directed *downwards* towards the axis of the fan, apparently drawn thither by the current. The flame was about 2 cm. long and formed a sharp-pointed cone having the spark-gap (12 mm. in length) as its base. Occasionally, if the discharge were maintained, a fine filament of flame darted rapidly over a distance of a few cm. towards the fan. The speed of the fan was now reduced to about 30 revolutions per second and a discharge passed across the gap. The sequence of events was too rapid to be followed by the eye. It was observed that a downward-pointing tongue of flame was produced as before, and that this tongue, after some hesitation, shot towards the axis of the fan ; the whole vessel then seemed to fill with flame and the glass was shattered into powder.

Further experiments were made with mixtures containing less methane. On two occasions the globe was shattered owing to the

* No doubt owing to an unequal setting of the blades of the fan.

rapidity with which the mixture contained in it was inflamed, but in a number of experiments, notably in several with a mixture containing 5·0 per cent. of methane (see T., 1914, **105**, 2595), the movement of the flame could be followed; or, at all events, owing to the persistence of retinal impressions, the course taken by the flame was apparent. An attempt has been made to indicate the appearance of the flame to the eye at a given instant by the shaded additions to Fig. 1. The impression produced can be described as that of a spiral whirlwind of flame, the axis of the spiral being inclined at an angle; in effect, the flame seemed to follow the course of the current induced by the fan. It appeared also that the flame passed several times through the mixture before it finally died away at the centre of the sphere. Analysis of the products of combustion of the 5·0 per cent. mixtures of methane and air showed that all the methane had been burnt.

There can be little question, as a result of these observations, that the action of the form of turbulence studied in causing an enhanced speed of combustion of a weak inflammable mixture of methane or ethane and air within a closed vessel is purely mechanical. The flame, which normally would be propagated mainly by conduction of heat from a burning to an unburnt "layer" of mixture, is forcibly dragged in the wake of the rapid current induced by the fan, burning the mixture in its path. The difficulty experienced by the flame in such weak mixtures in travelling away from the source of ignition if the speed of the fan is very great is no doubt due to the fact that mixtures of the paraffins with air exhibit a considerable "time-lag" when the temperature of the source of heat that causes ignition is but little above the ignition-temperature, a condition obtaining with the flames of limit mixtures.

With richer mixtures, in which flame normally spreads at an equal speed in all directions from the source of ignition, the action of turbulence is mechanical also. To quote Mallard and Le Chatelier (*loc. cit.*, p. 350):

"Lorsque le gaz dans lequel progresse la flamme est à l'état d'agitation, la vitesse de propagation augmente parceque la chaleur se transmet non seulement en vertu de la conductibilité du mélange gazeux, mais encore en vertu des différences de vitesse des diverses parties de la masse. La surface de la flamme, au lieu de garder une forme constante et régulière, se deforme à chaque instant, augmente de largeur en multipliant les points d'inflammation et, par suite, en rendant plus rapide la progression de la combustion."

If this explanation is correct, it follows that (1) the greater the turbulence the more rapid should be the combustion; and (2) a

FIG. 1
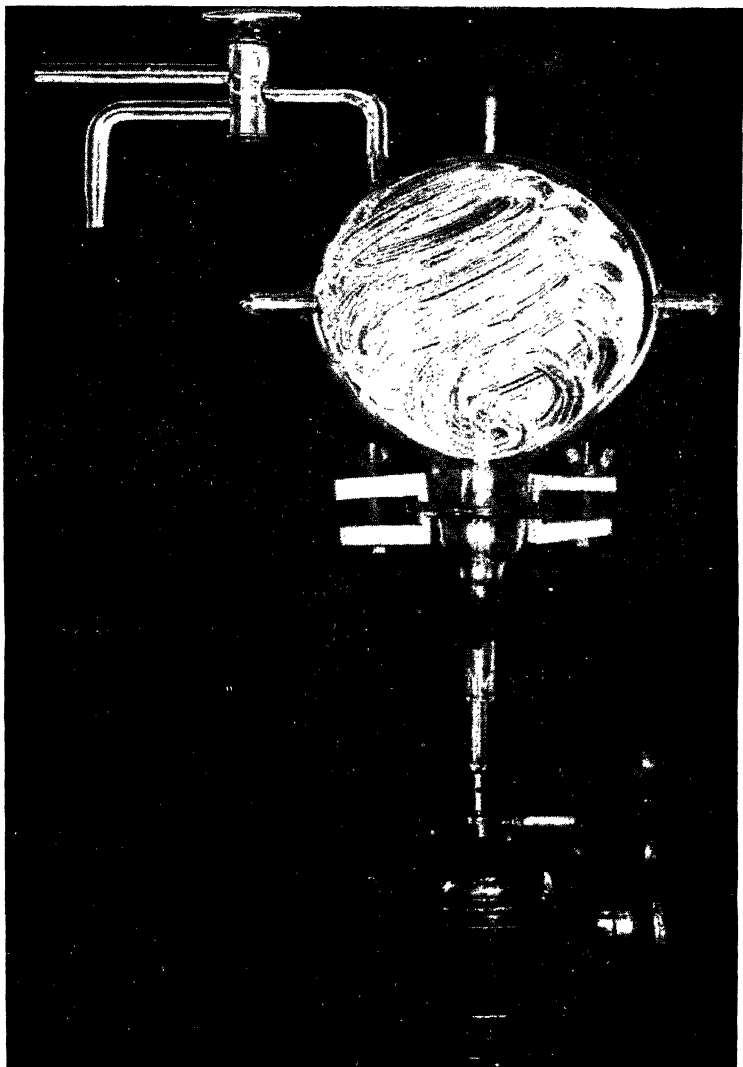
mixture in which the speed of flame normally is slow should be more susceptible to the effects of turbulence than one in which the speed of flame normally is rapid.

The first deduction has received experimental verification by Hopkinson, whose results have already been quoted. His results are confirmed by a series of experiments in the 4-litre sphere with mixtures of ethane and air containing 3·85 per cent. of ethane, the time-pressure curves for which are reproduced in Fig. 2. The time-intervals between ignition and the attainment of maximum pressure were: mixture at rest, 0·146 sec.; fan running at (a) 20 revs. per sec., 0·091; (b) 40 revs. per sec., 0·070 sec.; (c) 100 revs. per sec., 0·045 sec. Additional points that should be

Fig. 2.

Time, seconds. Time 0 = time of ignition.
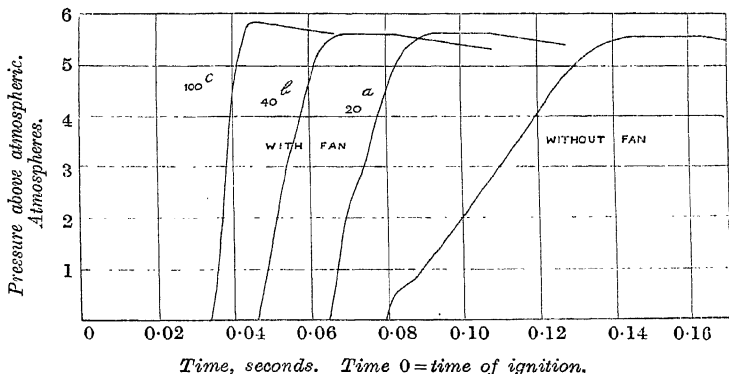
noted as regards these curves are: (1) the slight increase of pressure obtained with the turbulent mixtures (a) and (b), and the marked increase with the turbulent mixture (c) as compared with that produced by the quiescent mixture; and (2) the disappearance from the curve for turbulent mixture (c) of the horizontal portion at maximum pressure noticeable in the other three curves. An explanation of these effects is offered later.

In order to test the second deduction that should follow if the explanation suggested for the action of turbulence is correct, two series of experiments were made with mixtures of ethane and air ranging between the lower-limit mixture and that giving the maximum pressure on combustion. In the one series the fan was run at a constant speed of 100 revolutions per second; in the other the

fan was at rest. The time–pressure curves for typical experiments of these two series are shown in Figs. 3 and 4,* the curves for the

FIG. 3.

Time, seconds. Time 0 = time of ignition.

FIG. 4.

Time, seconds. Time 0 = time of igniton.
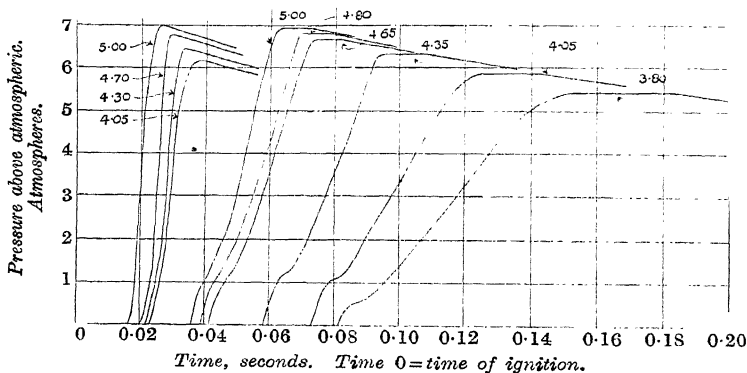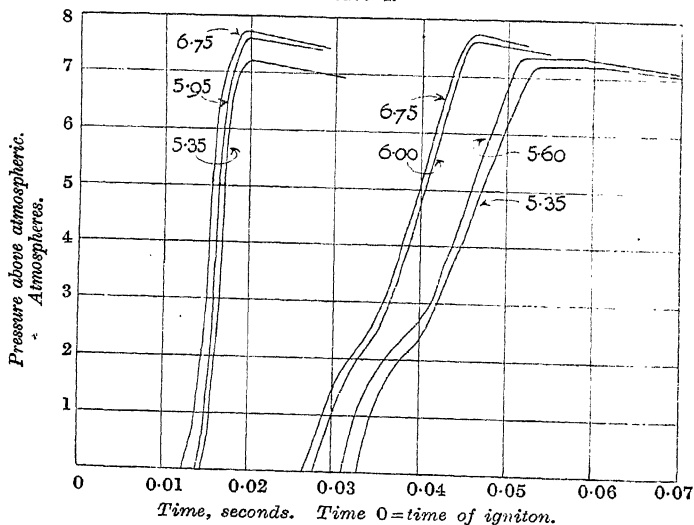
* It should be noted that the unit of time employed in plotting the curves in Fig. 3 (and Fig. 2) is double that in Fig. 4. This contraction of the time-scale is rendered necessary from considerations of space.

turbulent mixtures occupying the left-hand portion of each diagram.

From these curves the time that elapsed between ignition and the attainment of maximum pressure for each mixture can be determined. These times, together with the times for mixtures not included in Figs. 3 and 4, are recorded in the table that follows:

Ethane in mixture. Per cent.	Time between ignition and the attainment of maximum pressure. Seconds.	
	Without turbulence.	With turbulence.
3·30	—	0·176
3·45	—	0·096
3·60	0·332	—
3·80	0·152	—
3·85	0·146	0·045
4·05	0·124	0·036
4·30	—	0·033
4·35	0·094	—
4·60	—	0·026
4·65	0·073	—
4·70	—	0·029
4·80	0·070	—
5·00	0·063	0·024
5·25	—	0·021
5·35	0·054	0·020
5·60	0·052	—
5·95	—	0·019
6·00	0·0465	—
6·40	—	0·019
6·45	0·046	—
6·75	0·0465	0·019
7·05	0·050	0·020
7·15	0·052	—

It has been shown (T., 1918, **113**, 852) that these time-intervals can be used to calculate, for each mixture, the mean speed of propagation of flame between the centre and the top of the sphere, a distance of 9·75 cm. The speeds thus calculated are shown plotted against percentages of ethane in Fig. 5. Allowing for the irregularities, which are naturally more noticeable with the turbulent than with the quiescent mixtures, the speeds for equivalent percentages of ethane in the two sets of experiments, as deduced from the smoothed curves, are given in the table on p. 90.

The conclusion that a mixture in which normally the speed of flame is slow should be affected by turbulence to a greater extent than one in which normally the speed of flame is rapid is thus proved experimentally by the gradual diminution in the value of the ratio B/A.

The Development of Pressure.—On referring to the time–pressure curves for mixtures without turbulence given in Figs. 3 and 4, and

FIG. 5.
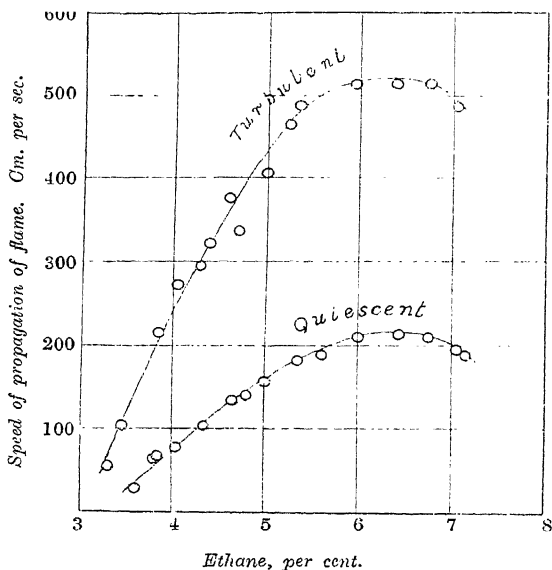
Ethane, per cent.

comparing them with the curves for mixtures of methane and air previously published (*loc. cit.*, Fig. 2, p. 847), it will be seen that

Mean Speed of Propagation of Flame from Centre to Top of Sphere. Cm. per sec.

Ethane in mixture. Per cent.	Without turbulence. (A).	With turbulence. (B).	Ratio B/A
3·6	35	142	4·06
3·8	55	195	3·54
4·0	75	237	3·17
4·2	95	284	2·99
4·4	112	320	2·85
4·6	129	360	2·79
4·8	144	400	2·77
5·0	158	430	2·72
5·2	172	462	2·68
5·4	185	485	2·62
5·6	195	500	2·56
5·8	202	510	2·52
6·0	210	518	2·47
6·5	212	518	2·44
6·7	200	495	2·47

both sets of curves are of the same type. All the mixtures of

ethane and air up to and including that containing 5·6 per cent. of ethane have time–pressure curves which exhibit the three stages of development noticeable with the mixtures of methane and air. The explanation of these stages offered when describing the methane curves can be applied also in the present instance.

Support is given to the assumption then made that the second stage of development, during which the recorded pressure remains constant, represents a balance between a gradual decrease of pressure that begins as soon as inflammation of the mixture is complete and is due to cooling by the walls of the vessel, and an increase of pressure incident at the same moment and due to the gradual attainment of thermal equilibrium. For it will be found that a graphical "correction" applied, in conformity with this assumption, in the manner described (*loc. cit.*, p. 849) yields results for the maximum pressures in close agreement with the maxima recorded by equivalent mixtures when turbulent, over the whole range from 3·80 per cent. ethane (at and above which percentage the flame travels from the centre in all directions at the same speed) upwards.

This is best shown in Fig. 6, where the observed maximum pressures for all the mixtures experimented with, both turbulent and quiescent, and the "corrected" maxima for the latter, are shown plotted against percentages of ethane. It should be observed that the magnitude of the correction, as is to be expected, diminishes in proportion as the speed of inflammation of the mixture increases. Similarly, the magnitude of the difference between the maximum pressures recorded with like mixtures when turbulent and quiescent also decreases as the speed of inflammation of the latter increases, until with mixtures containing more than 5·6 per cent. of ethane no difference is observable between the two sets of pressures. Further, the crests of the time–pressure curves for the quiescent mixtures that contain more than 5·6 per cent. of ethane no longer remain horizontal over a measurable length of time, but the cooling curves begin as soon as the maxima are attained.

Pier (*Zeitsch. Elektrochem.*, 1909, **15**, 536), who used the pressures developed by the inflammation of different mixtures in a closed vessel to determine the specific heats of various gases, has made observations which have a bearing on the question of the effects of turbulence.

Using a manometer of similar construction to the Petavel gauge (*Phil. Mag.*, 1902, [vi], **3**, 461), Pier found exact agreement between the observed and the calculated pressures produced by mixtures the combustion-temperatures of which exceeded 1600°. For this reason he combatted Nagel's opinion ("Versuche über Zundgeschwindig-

heit explosibler Gasgemische," *Mitteilungen über Forschungs-arbeiten des Ingenieurwesens*, Vol. 54, 1908) that with central ignition in a spherical vessel the mixture near the walls must be raised in temperature by adiabatic compression before flame reaches it

FIG. 6.

Ethane per cent.

Quiescent, observed   ×
      ,,   corrected   ●
Turbulent, observed   ○
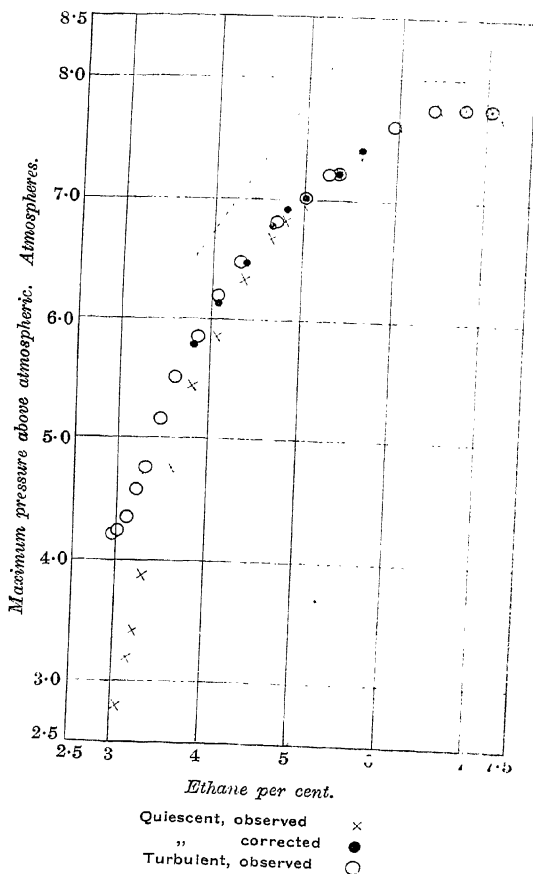
(an opinion that had already received experimental verification by Hopkinson), and suggested that the interchange of heat between different portions of the mixture within the vessel must be practically instantaneous.

This result Pier supposed would be effected by a rapid whirling and mixing of the contents of a spherical vessel owing to a sudden increase of pressure on ignition at the centre. It is clear, if only by reason of the difference observable in the character of the time–pressure curves for ethane–air mixtures with and without artificially-produced turbulence, that Pier's contention cannot be correct; and Hopkinson's measurements of the temperatures within a closed cylindrical vessel at the moment of maximum pressure produced by the inflammation of a mixture of coal-gas and air (*Proc. Roy. Soc.*, 1906, [*A*], **77**, 387) should have convinced Pier of its falsity.

In the absence of knowledge regarding the composition of the products of combustion at the moment of attainment of maximum pressure when the ethane–air mixtures contain excess of ethane, it is not possible to calculate the theoretical pressures that should be given by such mixtures on ignition in a closed sphere were there no loss of heat during the propagation of flame. Calculation can, however, be made for those mixtures in which the combustion of ethane can be presumed to be complete. The mixture of ethane with air in which ethane and oxygen are in the theoretical proportions for complete combustion to form carbon dioxide and steam contains 5·63 per cent. of ethane. The dotted line in Fig. 6 represents the calculated maximum pressures over the range 3·8—5·5 per cent. ethane.* It will be seen that a loss of heat of between 9 and 12 per cent., presumably due to radiation during the propagation of flame, is indicated.

A matter for further study is the fact that the mixtures of ethane and air which produce the highest pressures are not those within close range of the mixture containing ethane and oxygen in theoretical proportions for complete combustion (5·63 per cent. of ethane), but lie over a considerably higher range, namely, 6·5—7·0 per cent. The time taken for the attainment of maximum pressure reaches a minimum over the same range, or, in other words, the speed of propagation of flame under the conditions of the experiments is fastest in mixtures containing between 6·5 and 7·0 per cent. of ethane. In this respect the results obtained with mixtures of ethane and air differ markedly from those with methane and air.

Further comparison of these results with those obtained with mixtures of methane and air is reserved for a future communication, which will include the results of similar experiments with other members of the paraffin series of hydrocarbons.

* The calculations were made in the manner described in T., 1918, **113**, 858, using Langen's values for the specific heats of the gases.

EXPERIMENTAL.

The apparatus used (4-litre sphere) and general method of procedure for the experiments has already been described (*loc. cit.*, p. 854). The ehane was prepared by the action of water on zinc ethyl and was purified by liquefaction by liquid air; the ratio C/A on explosion analysis was $1·25$, showing that it contained no impurity.

The majority of the experiments described in this paper were carried out during the year 1912, with the assistance of Mr. M. J. Burgess.

IX.—*The Ignition of Explosive Gases by Electric Sparks.**

By JOHN DAVID MORGAN.

SOME time ago an investigation was carried out by Dr. R. V. Wheeler and Prof. W. M. Thornton on the ignition of explosive gases by sparks produced in signal bell circuits (Home Office Report on Electric Signalling with Bare Wires, R. V. Wheeler and W. M. Thornton, June, 1916). They used iron-core coils, in conjunction with mechanical means for breaking the circuit Commenting on the results obtained, they state:

"It may be said that ignition by a rapid break flash at a low circuit voltage depends on the inductance voltage at which the flash is formed, and the igniting power of the flash is proportional to the product Li (where L is the inductance of the circuit and i the current prior to breaking the circuit). When the break of the circuit is made slowly, the igniting power of the flash has been found to depend upon its energy, $\frac{1}{2}Li^2$. There are thus two limiting conditions for the igniting power of the flash; at the one the inductance voltage is of importance, at the other the energy. For any given gaseous mixture there is a range of rapidity of break over which the two types of ignition blend, so that under certain conditions the igniting power of the flash may be proportional

neither directly to i nor to i^2, but to some intermediate value of it."

Then, referring to a previous report (Home Office Report on Battery Bell Signalling Systems, R. V. Wheeler, January, 1915), they cite a case in which it was found that the igniting power of the break flash could be expressed by the relationship $Li^{1\cdot4} =$ constant.

The figures by Wheeler and Thornton in support of the conclusion that Li is constant are given in table I.

TABLE I.

Inductance (L). Henries.	Igniting current (i) at 25 volts. Ampere.	Li.
0·27	0·82	0·220
0·47	0·45	0·212
0·70	0·26	0·182
0·90	0·20	0·180
1·04	0·17	0·177
1·18	0·155	0·183
1·27	0·145	0·184
1·31	0·13	0·170
1·60	0·11	0·176
2·00	0·09	0·180

In the same report they give the number of layers of wire on the magnets used by them, together with the igniting currents. These are given in table II. I have added a third column giving the product N^2i^2, where $N =$ number of layers. As the layers each have the same number of convolutions, N is proportional to the turns. It will be noticed that it can also be said that N^2i^2 is constant, a quantity which has not the same physical significance as Li. The expressions are only comparable when each contains either of the terms i or i^2.

TABLE II.

Layers of wire on magnet (N).	Igniting current (i).	N^2i^2.
4	0·82	10·8
8	0·45	12·8
12	0·26	9·7
16	0·20	10·0
18	0·17	9·3
20	0·155	9·6
22	0·145	10·0
24	0·13	9·7
28	0·11	9·6
32	0·09	8·4

In the earlier report by Dr. Wheeler, a table is given from which the number of layers on the magnet coil can be deduced, and

the igniting current is added. Using these figures, I have calculated N^2i^2, and the figures are given in table III.

<div align="center">

TABLE III.

Number of layers (N).	Igniting current (i).	N^2i^2
20	0·17	11·6
16	0·23	13·6
12	0·33	15·6
8	0·55	19·2
6	0·95	32·5

</div>

The figures in the third column show that in this case the product N^2i^2 is by no means constant, but progressively increases.

When the flux produced by the current is linked with the whole of the windings, the product N^2i^2 is proportional to the electrokinetic energy of the system so long as the permeability is constant. When the linkage is imperfect or the permeability varies, the energy is not proportional to N^2i^2. From the results above referred to, it is found that when a low tension igniting spark is defined in terms of the coil constants (N or L) and the current (i) prior to the spark, the energy required to produce a spark that will ignite a gas mixture of given composition appears to be constant in some cases and not constant in others.

Experiments with low tension sparks have led me to suspect that such results as those above mentioned, though apparently diverse, have some constant factor in common, and that the disparities are due to the manner in which the results are expressed. There is not implied by this remark any suspicion of the accuracy of the work done by Wheeler and Thornton. They were concerned mainly with determining what circuit conditions could give rise to dangerous sparks, and from that point of view the results were expressed in terms of practical utility. The question raised is as to whether the results as expressed can be employed to determine the property of the spark on which ignition depends.

I therefore decided to make a new investigation with low tension sparks, and arrange the experiments to cover a wide range of different magnetic conditions. Six short air-core coils were made according to the particulars given in table IV.

<div align="center">

TABLE IV.

No.	Number of turns.	Number of layers
1	100	2
2	200	4
3	300	6
4	400	8
5	500	10
6	700	14

</div>

Two iron cores of relatively large cross-section were also made, one a laminated bar and the other a closed laminated frame, for use with the same coils. The experiments were divided into three groups, which were distinguished only by the differences in the magnetic conditions of the cores. Diagrammatic representations of the coils are shown in Fig. 1. Current was obtained from a 12-volt accumulator. The circuit was completed by a variable

FIG. 1.

Air-core coil

Open iron-core coil.

Closed iron-core coil.

resistance of negligible inductance, an ammeter, and a 'flick' contact breaker, the latter being enclosed in the explosion chamber. The contact breaker consisted of a flexible steel prong capable of being rotated into contact with a fixed steel stem, and then flicked over the stem. A coal gas and air mixture of constant composition was used throughout the investigation.

The least currents required to produce ignition are given in table V.

TABLE V.

Air-core Coils.

No. of layers (N).	Current (i) amperes.	N^2i^2.
2	4·5	81
4	2·05	67·4
6	1·2	54
8	0·83	44
10	0·575	33
14	0·35	24

Open Iron-core Coils.

No. of layers (N).	Current (i) amperes.	N^2i^2.
2	1·05	4·4
4	0·51	4·3
6	0·35	4·4
8	0·26	4·3
10	0·21	4·4
14	0·15	4·4

Closed Iron-core Coils.

No. of layers (N).	Current (i) ampere.	N^2i^2.
2	0·63	1·6
4	0·32	1·64
6	0·2	1·44
8	0·16	1·64
10	0·13	1·69
14	0·09	1·6

Figs. 2 and 2a give the results graphically.

It will be noticed that the product N^2i^2 is not constant for the air-core coils, although it tends to a constant value at the upper value of N, and is constant with the open iron and closed iron-core coils, although the value of N^2i^2 is different in the latter two cases.   In other words, the results may be said to be similar in kind to those obtained in Wheeler and Thornton's investigations.

The present investigation differs from those as recorded in the cited reports of Wheeler and Thornton, in that I have carried out measurements on the circuits after interruption.   The first step consisted in the use of an arrangement as shown in Fig. 3.   This is a Wheatstone bridge in conjunction with a ballistic galvanometer.   The inductance coil a, non-inductive balance resistance b, ammeter c, flick contact breaker d, variable non-inductive resistance e, and battery f are all (excepting b) as used in the explosion experiments. a and b are shunted by non-inductive resistances r of sufficiently low resistance to eliminate sparking at d when the circuit is broken.   Using with each coil the current values required

to give the igniting sparks, the observed "kicks" were plotted against N. These are given in Fig. 4. The straight lines indicate that for each group the energy associated with the system prior to interruption was constant, but they give no information as to

FIG. 2.

a	b	i c
6	1·2	0·6
5	1·0	0·5
4	0·8	0·4
3	0·6	0·3
2	0·4	0·2
1	0·2	0·1

$a = $ air-core coil.
$b = $ open iron-core coil.
$c = $ closed iron-core coil.

FIG. 2a.

$a = $ air-core coil.
$b = $ open iron-core coil.
$c = $ closed iron-core coil.

E 2
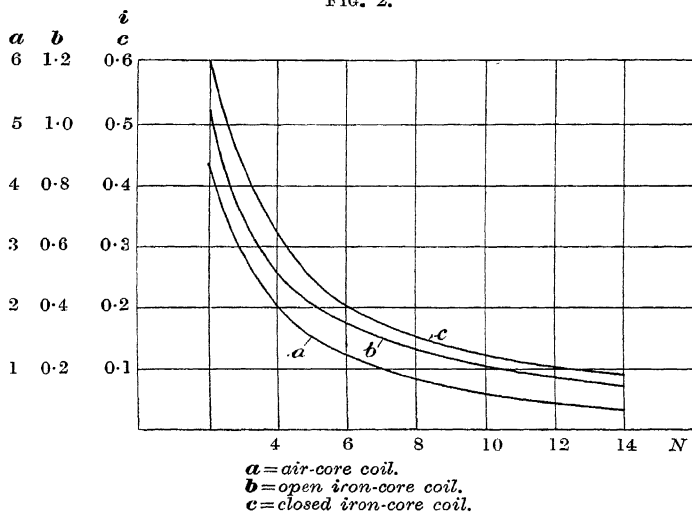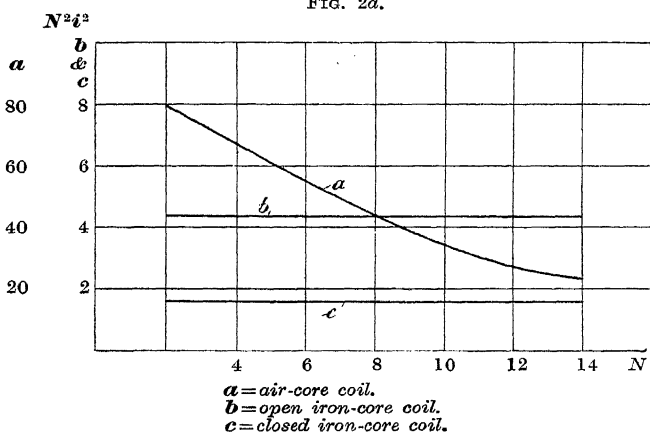
whether the energy was the same for each group. The induct-
ances were therefore measured, and found to give $\frac{1}{2}Li^2 =$ constant
for each group, but different for different groups. As nothing is
gained by quoting all the values of all the inductances, only the
largest for each group is recorded in table VI.

<div align="center">TABLE VI.</div>

	$L.$	$\frac{1}{2}Li^2.$
Air-core coil, 14 layer	0·01	0·0006 joule.
Open iron-core coil, 14 layer	0·07	0·0008 ,,
Closed iron-core coil, 14 layer	0·56	0·0023 ,,

It is clearly not permissible to conclude that the energy pro-
jected into the sparks in the explosion experiments is constant for
a constant magnetic condition, but different when that condition

<div align="center">FIG. 3.</div>
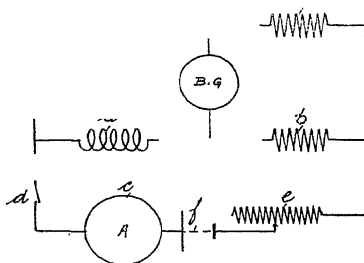
is changed, until it is proved that the differences found are not
accounted for by core or other losses. A further step, involving
direct spark measurements, was therefore necessary. After try-
ing various schemes, the apparatus shown diagrammatically in
Fig. 5 was adopted. a is the flick contact breaker used in the
explosion experiments. This is enclosed in an ebonite chamber,
b, to which a capillary tube is sealed. Two things appeared at
first to render this device useless. The heat developed by the
current passing through the contact breaker when closed was
sufficient to interfere with proper measurement of the heating
effect of the spark produced on opening the contact breaker.
Further, it was difficult to maintain a perfectly gas-tight joint
around the rotatable stem carrying the prong of the contact
breaker. These troubles were avoided by permitting a slight leak
in the chamber and observing (through a microscope) only the
"kick" given to the liquid thread in the capillary tube. Using

the coils and current values employed in the explosion experiments, it was found that the "kicks" were the same throughout. It follows that the sparks obtained in the three widely varying groups of experiments were identical as regards their impulsive thermal effects.

I do not think it can be argued from the above that the spark

FIG. 4.

$a = air\text{-}core\ coil.$
$b = open\ iron\text{-}core\ coil.$
$c = closed\ iron\text{-}core\ coil.$
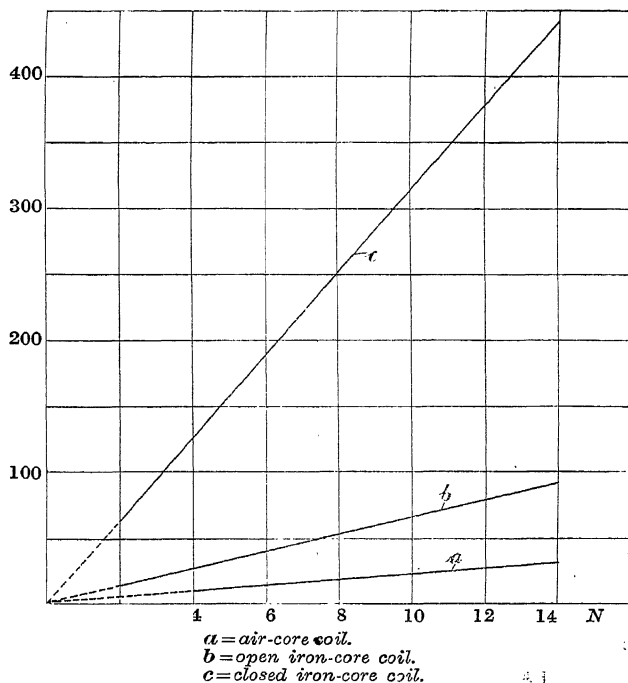
energy was the same in all cases, although this possibility is not excluded.

The final step consisted in an attempt to determine definitely whether the energies of the different sparks were the same or not. For this purpose, a high tension winding of fine wire and many turns was placed on one of the limbs of the closed iron core, as

shown in dotted lines, Fig. 1, and connected to a small, permanent
gap in a spark plug, *a*, Fig. 6.   The sparks produced were very
small, and several had to be produced in succession to give a
deflection definitely readable through the microscope.   In place of
the flick contact breaker in the primary circuit, a cam-operated
interrupter, such as is used in ignition apparatus for internal-
combustion engines, was employed.   With this interrupter, twelve

FIG. 5.
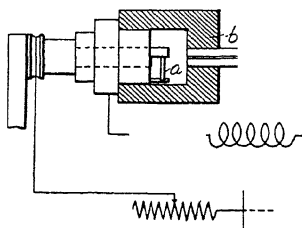
sparks were obtained from each complete rotation of the cam.
The chamber was made perfectly gas-tight, and the deflections
were different in character from those of the previous experiment
in that they were relatively slow.   Taking each of the coils in
turn and using the current values obtained in the explosion experi-
ments, the deflections obtained after one complete rotation of the
cam were observed.   In all cases they were found to be the same.

FIG. 6.
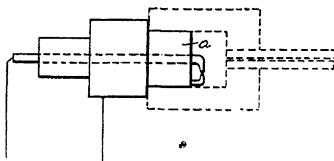
It follows that the total heating effect of the same number of
sparks from each coil was the same ; consequently, the sparks were
of equal energy.   Seeing that the sparks in all three groups of
experiments gave the same impulsive thermal effects and the sparks
in one group gave the same energy effects, it is permissible to argue
that the energies of all the sparks in the three groups were the
same.

The conclusion of the investigation is therefore that over the wide range of different conditions examined, the igniting sparks had this in common—that they all liberated the same amount of heat energy, a result which is not evident from measurements on the spark circuit prior to the production of the sparks.

Regarding single spark ignition of explosive gases initially at atmospheric temperature and pressure, the main results of investigations which have been published in recent years, and which can be regarded as well established, appear to be as follows:

(1) With a low tension spark, the least spark energy required to ignite a given gas mixture diminishes with increase of the voltage impressed on the spark circuit prior to the production of the spark (The least energy required to start a gaseous explosion, W. M. Thornton, *Phil. Mag.*, 1914, [vi], **28**, 734).

(2) When the circuit voltage is constant, the spark energy required for ignition of a given gas mixture by a low tension spark is constant (see above).

(3) With a high tension spark (which consists of a capacity component preceding an inductance component), the incendivity of the spark (or ability to cause ignition) can be increased by increasing the proportion of energy in the initial part of the spark without increasing the total energy of the spark ("Spark Ignition," J. D. Morgan, *Engineering*, November 3rd, 1916).

(4) The incendivity of a condenser or capacity spark is greater than that of an inductance spark dissipating the same amount of energy (Thornton, *loc. cit.*).

(5) With a capacity spark, the least energy required for ignition of a given gas mixture diminishes as the spark voltage increases (Thornton, *loc. cit.*).

These results clearly establish the fact that the incendivity of a spark does not depend on the total energy of the spark.

It is generally supposed that the energy required to produce ignition of a given inflammable gas mixture is constant for similar physical conditions. If the assumption is correct, then the fact that the total energy of the least igniting spark is found experimentally to vary with the conditions under which the spark is produced suggests that not all of the spark energy is utilised in the process of ignition, but only a portion at the commencement of the spark. It is, of course, possible that the inflammability of a gas as determined by the least energy required to produce ignition is not constant for identical physical conditions of the gas, but it would appear to be useless to attempt an investigation of this point by spark measurements having regard to the facts above mentioned. It is important to note that a spark is a varying

source of heat which very rapidly reaches its maximum intensity and then less rapidly disappears. Experiments prove that increase of the initial intensity of a spark results in increased incendivity. As already stated, this suggests that ignition is due only to the initial part of the spark, and that in every spark there is a certain amount of unused energy which makes no contribution to the process of ignition. The proportion of unused energy must diminish as the initial intensity increases, but at present any measurements of the effective portion of the spark appear to be impossible. It follows from this suggested theory of unused energy that any attempts to specify the inflammability of a gas in terms of the total energy of the least igniting spark must necessarily yield the diverse results which have hitherto been obtained.

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X.—*The Physical Constants of Nicotine. Part I. Specific Rotatory Power of Nicotine in Aqueous Solution.*

By HARRY JEPHCOTT.

NICOTINE has been purified and its constants have been recorded by Landolt ("Optical Rotation of Organic Substances"), Nasini and Pezzolato (*Zeitsch. physikal. Chem.*, 1893, **12**, 501), Gennari (*ibid.*, 1896, **19**, 130), Hein (*Diss.*, Berlin, 1896), Přibram and Glücksmann (*Monatsh.*, 1897, **18**, 303), Ratz (*ibid.*, 1905, **26**, 1241), and Winther (*Zeitsch. physikal. Chem.*, 1907, **60**, 563). All, with the exception of Ratz, relied on the distillation in hydrogen of anhydrous nicotine. Ratz utilised two methods, namely, fractional distillation in a vacuum and the formation of nicotine zinc chloride followed by distillation. Their results for the specific rotation, which show considerable variation, are as follows :

	$[\alpha]_D^{20}$.	D_4^{20}.
Landolt	161·55	1·01101
Nasini and Pezzolato	161·29	—
Gennari	162·84	1·01071
Hein	164·18	1·01049
Přibram and Glücksmann	164·91	1·0095
Ratz (by fractional distillation)	166·77	—
,, (from double salt)	169·0 to 169·54	1·00925
Winther	163·85	—

It appeared probable that the variation was due to the presence of the alkaloids nicoteine, nicotelline, and nicotimine, which occur with nicotine, and it was decided to purify nicotine by the method utilised by Pictet and Rotschy (*Ber.*, 1901, **34**, 696) when isolating these alkaloids. Nicotine which had been prepared from tobacco by steam distillation was dissolved in a slight excess of hydrochloric acid and treated with sodium nitrite at low temperature. The nicotine was subsequently liberated by alkali, dehydrated, and fractionally distilled under diminished pressure. Considerable loss of nicotine occurred owing to the formation of oxidation products during the treatment with nitrite.

A quantity, about 2500 grams in all, of commercial nicotine was also converted into nicotine zinc chloride, twice recrystallised, and the nicotine liberated, dehydrated, and fractionally distilled under diminished pressure in a manner similar to that of Ratz (*loc. cit.*).

The distillation was a source of much trouble. In the cold, nicotine readily forms highly-coloured oxidation products on exposure to the air. When hot, this oxidation is extremely rapid, and water is also absorbed. At the temperature of distillation, the vapour readily attacks cork or rubber used for connexions. Well-fitting ground-glass joints are essential, but there proved to be no necessity to flood the apparatus with hydrogen if a sufficiently high vacuum were maintained (20—40 mm. pressure).

The nicotine prepared in this way was colourless and almost without odour in the cold. When kept in bottles filled to the stopper and away from the light, nicotine remains colourless, only the slightest yellow tint being noticed after six months and no change in rotatory power (compare Pribram, *loc. cit.*, p. 303).

For pure nicotine, the density and rotatory power were found to be as follows :

	D_4^{20}.	$[\alpha]_D^{20}$.
Purified through nitroso-compound	1·00920	168·52
Purified through double chloride (1) ...	1·00925	168·61
,, ,, ,, ,, (2) ...	1·00925	168·40
,, ,, ,, ,, (3) ...	1·00925	168·66

The three sets of figures for the double chloride method refer to three separate and distinct preparations of pure nicotine in that way.

Many dilutions of this nicotine with water were prepared, and the specific gravity and specific rotatory power for them observed. The rotations were measured with a Schmidt and Haensch half-shade polarimeter, using a tube having a length of 100·04 mm.

	Grams in 100 c.c.	D_4^{20}.	$]_D^{20}$.	Percentage by weight.	Gr in 100 c.c.	D_4^{20}.	$[α]_D^{20}$.
00	100·925	)0925	.68·61	44·004	45·296	1·02936	86·47
95·068	96·801	)1823	.53·06	41·718	42·882	1·02790	86·71
91·084	93·323	)2458	.41·65	40·237	41·308	1·02661	85·09
89·471	91·781	)2583	.38·73	38·798	39·804	1·02592	83·79
88·338	90·820	)2810	.34·11	38·065	39·025	1·02522	85·21
83·336	86·132	)3356	.23·21	37·986	38·950	1·02538	84·98
81·842	84·632	)3439	.21·48	35·098	35·920	1·02341	83·52
77·006	79·921	)3784	11·47	34·877	35·696	1·02351	83·39
75·538	78·551	)3836	08·39	32·141	32·810	1·02107	81·83
84·868	77·764	)3839	08·69	30·973	31·607	1·02048	82·48
69·202	71·963	)3990	00·47	30·637	31·253	1·02010	82·67
67·538	70·231	)3988		30·291	30·915	1·02060	82·60
64·423	66·918	)3890	97·82	28·151	28·664	1·01820	81·95
63·950	66·440	)3894	95·63	26·473	26·930	1·01725	81·78
60·773	63·110	)3846	94·02	24·975	25·369	1·01588	81·67
59·898	62·131	J3728	93·69	20·963	21·235	1·01300	80·64
59·649	61·895	·03765	95·12	20·726	20·995	1·01299	80·06
56·241	58·250	·03614	91·27	15·023	15·156	1·00880	80·99
54·289	56·245	·03603	89·27	12·963	13·027	1·00492	79·79
53·096	54·934	·03463	90·12	11·508	11·579	1·00611	79·43
51·969	53·750	·03428	86·91	.0·012	10·061	1·00611	78·66
50·134	51·777	·03278	89·03	9·921	9·971	1·00494	79·20
48·949	50·513	·03194	88·19	7·417	7·441	1·00317	79·94
46·632	48·062	·03065	86·23	6·604	6·622	1·00276	79·25
46·183	47·629	·03131		4·998	5·006	1·00153	80·48
46·015	47·412	·03037		2·505	2·504	0·99970	83·15

The effect of peratur density and rotatory power both of pure n otine and certain of its aqueous solutions has a been observed. For this purpose, a jacketed polarimeter tube

Nicotine in aqueous solution.

Specific rotation. / Density. / Percentage by weight.
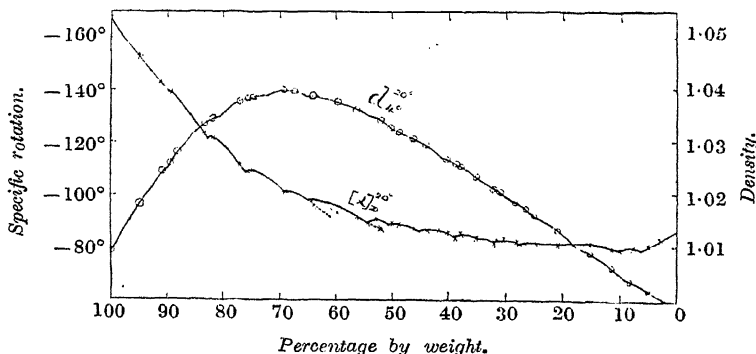
employed, a Sprengel tube being used for the densities. It was not convenient in every case to observe both density and angle at the same temperature, and the density at the temperature at

which the rotatory power was observed was obtained from a graph constructed from the recorded densities.

Pure Nicotine.

Temperature.	20°.	21·1°.	40°.	60°.	80°.	97·7°.
$D_4^{2^0}$	1·00925	1·00865	0·99424	0·97799	0·96184	0·94534

Temperature.	D_4^t (from graph).	$[\alpha]_D^t$.
20°	1·00925	168·20°
29·5	1·0017	168·71
41·5	0·9924	169·09
52	0·9840	169·51
62	0·9760	169·74
69·6	0·9699	169·94
86·4	0·9567	169·73
92·0	0·9521	169·71

Owing to the so-called closed curve of solubility of nicotine in water, it is not possible to observe the rotatory power and density of solutions containing between 7 and 87 per cent. of nicotine at all temperatures up to 100°, since separation occurs at about 60°. Two solutions were therefore prepared which would fall outside this closed curve, and contained 6·638 per cent. and 88·338 per cent. of nicotine. For these, the following figures were found:

Temperature.	Percentage by weight.	Grams in 100 c.c.	D_4^t.	$[\alpha]_D^t$.
20°	6·638	6·682	1·00275	76·82
85	6·638	6·4188	0·96328	95·29
20	88·338	90·820	1·02810	134·16
90	88·338	86·936	0·98412	150·34

It will be observed that the change in rotatory power is marked.

On cooling to 20°, the 6 per cent. solution at once showed its original rotatory power, but the 88 per cent. solution did not revert to its former value for some days, although an immediate fall to about $[\alpha]_D^{20}$ 138·0 took place. Difficulty occurs in determining the rotatory power of pure nicotine and its more concentrated solutions, since, owing presumably to light absorption, it is necessary to match a greyish-pink against a grey when taking polarimetric readings. In the case of the more concentrated aqueous solutions, the difficulty is greatly increased owing to the very marked changes in density. In observing the angle of the 88 per cent. solution at 90°, even with a rapid stream of water circulating round the jacket, the change in density by cooling at the exposed surface of the end plates was so marked as to make it almost impossible to get light to pass through the tube, and the

rotation recorded must be considered liable to an error of 1°. No such difficulties were experienced with the 6 per cent. solution.

The graphs for density and specific rotatory power of nicotine in aqueous solution both exhibit a series of maxima, and these agree with molecular proportions of nicotine and water. This indication of the formation of a series of hydrates is confirmed by an examination of the freezing points of nicotine solutions.

Between 40 and 80 per cent., the time taken for hydrate-formation is appreciable, and the abnormal points marked were found in cases of solutions when the rotation was observed immediately after mixing. A solution containing 69·2 per cent. of nicotine showed no change in rotation after keeping for twelve months.

The "Closed Curve of Solubility" for Nicotine.

The formation of hydrates of nicotine and their decomposition at higher temperatures shows the true nature of the "closed curve of solubility." Nicotine is only sparingly soluble in water, and water is only sparingly soluble in nicotine, but hydrates of nicotine are miscible with either, a state of balance existing at any given temperature between nicotine, its hydrates, and water.

When the temperature rises, the hydrate-formation reverses, and on the concentration of free nicotine becoming greater than the solubility of nicotine in water at that temperature, separation occurs. By choosing concentrations of nicotine and water such that the limit of solubility of the one in the other was not exceeded, it was possible, as shown above, to note the marked rise in rotatory power as the concentration of free nicotine increased with the rise in temperature, and it is to be expected that with convenience for observing the angle at a sufficiently high temperature, the true rotatory power of nicotine in water would be obtained.

XI.—*The Sub-acetate and Sub-sulphate of Lead.*

By Henry George Denham.

In recent papers the author has shown how lead sub-oxide may be converted into the sub-haloid salts by the action of alkyl haloid vapour (T., 1917, **111**, 29; 1918, **113**, 249); in the present paper a somewhat similar method has been used for the preparation of lead sub-acetate and sub-sulphate.

In all these experiments, the lead sub-oxide was prepared by the decomposition of pure lead oxalate according to the method previously described (*loc. cit.*). The same precautions have been followed in order to secure thorough preliminary heating of the reacting gases, the vapour being passed through a capillary spiral tube contained in the oven before it came in contact with the sub-oxide. The only modification necessary in the distillation has been that no drying agent was used in the apparatus, and it was necessary to heat electrically all the leading tubes in order to prevent undesired condensation and to secure a steady rate of distillation.

Preparation of Lead Sub-acetate.

Preliminary experiments were carried out with methyl acetate. About 10 c.c. of a carefully dried sample of this substance were distilled through about 0·75 gram of lead sub-oxide, the duration of the experiment being approximately ninety minutes. Analysis of the product indicated that at 310° the sub-acetate decomposes completely, metallic lead being formed, whilst at temperatures much below this, the reaction proceeded too slowly to appear promising. Ethyl acetate behaved similarly, and an experiment was then carried out with acetic anhydride.

Lead sub-oxide mixed with about four times its weight of powdered glass was prepared in two bulbs (for details, see T., 1917, **111**, 29), and the apparatus filled with oxygen-free nitrogen. About 8 c.c. of carefully fractionated acetic anhydride were distilled through the bulbs at 195°, as recorded on a standardised platinum thermometer. This slow distillation generally lasted about eighty to ninety minutes. The oven was then cooled to about 180°, and the apparatus was exhausted by means of a Sprengel pump. The bulbs were then sealed off and were available for analysis. By this

procedure, any trace of acetic anhydride could be removed from the bulb without causing any decomposition of the sub-acetate.

One difficulty still remained. Traces of water were found to be retained most tenaciously by the sub-acetate. A few samples which were quite free from moisture were prepared, but in general, although the ratio of lead to acetate in the compound agreed with the theoretical ratio for lead sub-acetate, from 1 to 3 per cent. of water was also present. The presence of the water was repeatedly verified by the action of heat, a liquid which rendered anhydrous copper sulphate blue being fairly readily expelled.

Traces of acetic acid were generally present in nearly all the samples of acetic anhydride used, and this probably accounted for the presence of water in the sub-acetate. However, as the anhydrous and the hydrated sub-acetate showed no difference in solubility and general properties, anhydrous acetic anhydride was used only in certain control experiments.

Found: $Pb = 77\cdot6$, $77\cdot9$, $77\cdot9$; $C_2H_3O_2 = 22\cdot3$, $22\cdot0$, $22\cdot2$.

$CH_3\cdot CO_2Pb$ requires $Pb = 77\cdot82$; $C_2H_3O_2 = 22\cdot18$ per cent.

In seven experiments made with acetic anhydride containing traces of acetic acid, the average of the analyses was $Pb = 75\cdot8$; $C_2H_3O_2 = 21\cdot5$. There is a possible hydrate of the formula $(CH_3\cdot CO_2Pb)_2,H_2O$ which contains $Pb = 75\cdot3$ per cent., and it appears probable that where acetic anhydride containing traces of acetic acid is used, the product is the hydrate, containing more or less of the anhydrous sub-acetate. Thus in two experiments, in which the same sample of acetic anhydride was used, after a distillation lasting ninety minutes, the percentage of lead was: (a) bulb 1, $75\cdot4$, bulb 2, $75\cdot2$; (b) bulb 1, $75\cdot1$, bulb 2, $75\cdot2$.

Properties of the Sub-acetate.

In order to obtain evidence of the existence of the sub-acetate, determinations of the conductivity of a saturated solution of the substance and of the normal dehydrated acetate were carried out in absolute alcohol at 25°. The apparatus and method previously described (loc. cit.) were again used in order that traces of oxygen might be excluded when the sub-acetate was used. The resistance of the alcohol was 90,000 ohms, whilst that of a saturated solution of the normal acetate was 4100 ohms, and of the sub-acetate, (a) 6100, (b) 6400, (c) 6000 ohms.

As further evidence of the existence of a definite sub-acetate of lead, experiments on the decomposition of the normal acetate and the sub-acetate were undertaken. A sample of the anhydrous

normal acetate was heated in a vacuum and the temperature slowly raised. At 200°, a very slow evolution of gas occurred, becoming rather brisker at 240°. The temperature was then kept constant and the pump kept in action for nineteen hours. Gas was still very slowly evolved, and it was found that the acetate had scarcely changed colour, and there was a considerable crop of long, white, needle-like crystals which had volatilised out of the bulb into the relatively cooler leading tube within the oven.

A sample of the sub-acetate was then similarly treated. At 200°, gas was slowly evolved, the evolution becoming brisker at 240°. After seven hours at 240°, gas was still being evolved slowly, and a small, volatilised band of white, amorphous, basic material was found outside the furnace, whilst the material in the bulb had undergone a marked change. It was now full of long, needle-like, greyish crystals. This change, from a finely crystalline, bluish-grey substance into a mass of grey, needle-like crystals, was very marked, as, too, was the entire absence of the volatilised, white, needle-like crystals obtained in the decomposition of the normal acetate. The behaviour on heating the different acetates in a vacuum is so different that it would be difficult to maintain the view that the sub-acetate is a heterogeneous mixture of metal and normal acetate, and these results, coupled with the different conductivity of the saturated solutions, must rather be held to confirm the view of the chemical individuality of the sub-acetate. The sub-acetate exhibits the same behaviour towards acids as other sub-salts of lead, namely, it is rapidly decomposed into metal and normal salt.

Lead Sub-sulphate.

Methyl sulphate was distilled through lead sub-oxide at 280° for about seventy-five minutes, the manipulation being similar to that already described for the sub-haloid salts of lead (*loc. cit.*). No difference in behaviour or in appearance was detected in the products prepared from lead sub-oxide or from the sub-oxide diluted with four times its weight of silica. On the other hand, when the distillation was carried out at 310°, and the silica omitted, the resulting grey mass was seen under the microscope to contain clusters of white crystals in a dark background, and was clearly heterogeneous.

In the sub-sulphate prepared according to the above method, the lead was estimated by conversion into lead sulphate, and the sulphate by treating the sub-salt with dilute nitric acid, evaporating to dryness, washing out the lead nitrate, and weighing the

residue in a Gooch crucible as lead sulphate. Owing to the presence of traces of carbonaceous matter, the precipitate was generally faintly grey until after gentle ignition.

Found: Pb = 81·25, 81·62, 81·30, 81·29; SO_4 = 18·65, 18·56, 18·80, 18·62.

$PbSO_4$ requires Pb = 81·18; SO_4 = 18·82 per cent.

Properties of the Sub-sulphate.

The action of acids on the sub-sulphate is similar to their action on the sub-haloid salts. A solution of ammonium acetate when boiled with the substance leaves a deposit of spongy lead. In order to test the chemical individuality of a saturated solution of the salt, determinations of the conductivity in water and alcohol at 18° were made. The resistance of the water was 27,000 ohms, whilst that of a saturated solution of lead sulphate was 3030 ohms, and that of the sub-sulphate was (a) in air, 3100 ohms, and (b) in a vacuum, 3200 ohms.

The difference is so slight that it appears highly probable that there is decomposition into lead and lead sulphate, although no visible change occurred in the appearance of the residue.

The resistance of the alcohol was 90,000 ohms, whilst that of a saturated solution of lead sulphate was 93,000 ohms, and of the sub-sulphate 75,000 ohms.

Although a much more marked difference was obtained, the evidence afforded by the conductivity method was still so inconclusive that further evidence as to the individuality of the salt was sought by investigating the influence of temperature on the sub-sulphate. Were the substance a heterogeneous mixture of lead and lead sulphate, a rise in temperature above the melting point of lead would be expected to cause a pronounced change in the appearance of the finely divided lead. Before heating the sample, some of it was carefully observed under the microscope, and no sign whatever of heterogeneity was noticed, but the whole appeared a uniform iron-grey. The temperature was raised 120° above the melting point of lead for a period of four hours. On cooling, the microscope failed to reveal any change whatsoever in the appearance of the salt. The entire absence of anything in the nature of minute globules of lead certainly supports the contention that this greyish substance is definitely lead sub-sulphate.

Conclusion.

(1) Lead sub-acetate has been obtained by the action of acetic anhydride on lead sub-oxide at 195°.

(2) The substance is bluish-grey, and behaves similarly to other sub-salts of lead.

(3) Its solubility in alcohol differs slightly from that of the normal acetate, but the behaviour of the two acetates on heating in a vacuum supports the view of the chemical individuality of the sub-acetate.

(4) The sub-sulphate has been prepared by the action of methyl sulphate vapour on the sub-oxide at 280°.

(5) The substance is dark grey; conductivity experiments indicate that it decomposes on solution in water, but it appears more soluble in alcohol than does the normal sulphate.

(6) On heating the substance 120° above the melting point of lead, no change in its appearance could be detected or any sign of globules of lead.

In conclusion, the author begs to thank the Walter and Eliza Hall Trust for the facilities placed at his disposal for the prosecution of this work.

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XII.—*The Synthesis of Ammonia at High Temperatures. Part III.*

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IN previous communications (T., 1918, **113**, 168, 386), some account has been given of the formation of ammonia in a rapidly cooled high-tension arc and in water-cooled flames, and evidence has been brought forward to show that the percentage of ammonia in equilibrium with nitrogen and hydrogen, after decreasing with increasing temperature, passes through a minimum value, and at very high temperatures increases with increasing temperature, a result which may also be shown thermodynamically.

A determination of the equilibrium ammonia-content at the temperature of the high-tension arc (*J. Soc. Chem. Ind.*, 1918, **37**, 232) gave approximately 1·7 per cent. by volume for the equilibrium percentage at atmospheric pressure under the experimental conditions employed, and yields of ammonia up to 1·5 per cent. could be recovered by suitable cooling.

This reversal in the direction of variation of the equilibrium ammonia-percentage with temperature appears to be sufficiently interesting to justify further study, and it is proposed in the present paper to deal with the formation of ammonia in an arc of larger size and more usual character than those hitherto employed.

For the production of the arc, single-phase, 50-cycle alternating current supplied at a maximum potential of 375 volts was transformed to high tension by means of an oil-immersed static transformer having a step-up factor of 31·5.

It was found easily possible to obtain an appreciable concentration of ammonia by almost any method by which the mixture of nitrogen and hydrogen was brought into contact with the arc flame with subsequent rapid cooling, for instance, by means of a blown arc similar to that used by McDougall and Howles (*Proc. Manchester Phil. Soc.*, 1900, **44**, No. 13) for the synthesis of nitric oxide, but in such cases a considerable proportion of the gas mixture blown into the arc failed to reach the requisite uniform high temperature, and for a preliminary study of the maximum percentage of ammonia formed, as distinguished from the maximum quantity formed with a given expenditure of electrical energy, it was considered preferable to allow the arc to burn freely in the reacting gas mixture and to draw off samples of gas by means of a silica tube of small diameter placed in close proximity to the arc.

The latter part of the present paper was carried out with a view to bringing additional evidence that the formation of ammonia at high temperatures really takes place by the direct union of hydrogen and nitrogen, and not by the subsequent reduction of nitric oxide formed from traces of oxygen in the reacting

It should, further, be stated in this connexion that the mixture of nitrogen and hydrogen employed in all experiments reported both in this and in the previous papers was as far as possible free from oxygen, and in no case contained sufficient of this to account for such secondary formation of any appreciable part of the ammonia obtained.

E X P E R I M E N T A L.

The apparatus employed is shown in the figure.   The electrodes *A* and *B* are of platinum, and terminate in small spheres slightly more than 1 mm. in diameter.   *C* is a thick-walled capillary silica tube, its upper end being opened out and flattened so as to form a slit approximately 4 mm. long and 1·5 mm. wide.   The silica

wall bounding the ends of this was ground away, and in the depressions thus formed at each end of the silica slit, the electrodes rested, the lower part of the tube being circular in section and about 1·5 mm. in internal diameter.

The arc was enclosed in a large inverted flask provided with a side-tube and three-way tap, D, for preliminary exhaustion and subsequent admission of the gas to be subjected to the action of the arc, this gas normally passing into the flask at D and leaving the system by way of the silica tube already described.

For the following measurements, the current employed for arc-formation was limited by the interposition of an adjustable resist-ance on the low-tension side of the transformer.

The platinum electrodes became quickly white hot and the arc flame burned steadily across the slit, and was, to a certain degree, drawn into the tube by the current of gas. Sufficient cooling for the recovery of the greater portion of the ammonia formed and for the prevention of the fusion of the silica tube was obtained without water-cooling, provided that a thick-walled silica capillary was used and that the arc employed was not too large.

Samples of gas, taken at various rates, were analysed by passage through $N/10$-acid, and in some cases by allow-ing a small volume to pass through Nessler's solution, practically identical results being obtained from each method of analysis.

The quantity of ammonia observed is influenced necessarily, not only by the temperature of the arc, but also by heating and cooling factors. With very slow currents of gas, heating to arc temperature occurs satisfactorily, but the ammonia formed undergoes considerable decomposition owing to the slowness with which it leaves the region of maximum tempera-ture. Passage of the gas too quickly through the arc results in imperfect heating, such rapid passage, however, involving rapid cooling, and consequently a more complete retention of the ammonia formed.

It will be seen from table I that the concentration of the ammonia recovered at the ordinary temperature first of all rises rapidly with increasing velocity of passage, then passes a maximum
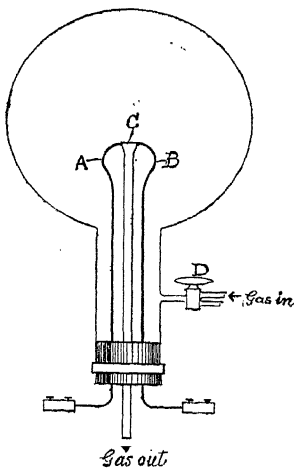
value, the percentage of ammonia subsequently falling gradually
with still greater velocities of passage.   This form of the concentra-
tion–velocity curve is a necessary result of the nature of the heat-
ing and cooling factors discussed above.

The issuing gas, of course, had a strong odour of ammonia at all
the rates of flow studied, and the percentages obtained were of the
same order of magnitude as those previously observed with small
arcs not produced directly by a high-tension current of the usual
sinusoidal wave form.   For this series of experiments, 0·04 ampere
at a potential of 3250 volts was taken for arc-formation.

TABLE I.

Nitrogen, 25 per cent.; Hydrogen, 75 per cent.

Rate of flow of gas in litres per hour.	Concentration of ammonia per cent. by volume.	Rate of flow of gas in litres per hour.	Concentration of ammonia per cent. by volume.
0·5	0·49	3·4	0·49
0·57	0·6	(3·4	0·45)
0·85	1·2	4·6	0·43
1·14	1·04	6·1	0·40
2·1	0·58	7·5	0·36
(2·1	0·56)	(7·5	0·32)

It appears desirable at this point to discuss the evidence that
the formation of ammonia at high temperatures takes place by the
direct union of nitrogen and hydrogen, and not secondarily by the
reduction of nitric oxide formed from nitrogen and traces of
oxygen in the reacting gas.   The point is of fundamental import-
ance in any consideration of the variation of the ammonia equil-
ibrium with temperature, and for this reason has been examined in
such a way as to place beyond doubt the direct nature of the
synthesis of ammonia at arc temperatures.

It may easily be shown from a consideration of the nitric oxide
equilibrium, particularly on account of the small partial pressure
of the nitrogen in the gas mixture employed, such mixture consist-
ing uniformly of 25 per cent. of nitrogen and 75 per cent. of
hydrogen, that a trace of oxygen, amounting to 1 per cent. by
volume or less, will not account for the percentage of ammonia
obtained, even assuming that all the nitric oxide which can be
formed under the conditions of experiment is quantitatively
reduced to ammonia.   The amount of nitric oxide that can be
formed from nitrogen and oxygen at partial pressures of the order
mentioned is depressed, by the ratio of partition of oxygen between
hydrogen and nitrogen, to a very small fraction of the already

small percentage which may be calculated as capable of being formed from a consideration of the nitric oxide equilibrium only.

In spite, however, of the small order of magnitude of the percentage of ammonia that might be formed secondarily from the traces of oxygen which are always present in commercial gases, it was considered preferable, both for the work described in the present paper and for all measurements of the formation of ammonia at arc temperature previously reported, to employ a gas known to be free from oxygen within the limits of the ordinary methods of analysis.

This gas was prepared in a manner similar to that used by Haber and Van Oordt (*Zeitsch. anorg. Chem.*, 1905, **44**, 341) for their determinations of the ammonia equilibrium at lower temperatures in the presence of a catalyst, by decomposing ammonia by passage through a heated iron tube, the mixture of nitrogen and hydrogen produced being carefully and thoroughly freed from ammonia by treatment with sulphuric acid and compressed for convenience into a previously exhausted steel cylinder by means of a totally immersed compressor of such design as to render impossible any penetration of air to the gas during compression. Each cylinder of nitrogen and hydrogen prepared in this way was carefully tested for absence of ammonia before use, by bubbling a considerable volume through Nessler's solution. The gas-mixture contained certainly less than 0·1 per cent. of oxygen, from which percentage the ammonia capable of being formed secondarily would be negligible, and in any case incapable of accounting for a yield of ammonia of 1 per cent. or more.

In a few preliminary measurements, a gas was used which had been made by the catalytic removal of traces of oxygen from a mixture of commercial hydrogen and nitrogen by passage over a heated metal, but whilst the resulting gas was equally satisfactory from the point of view of the yield of ammonia obtained by passage through an arc, the preparation of an oxygen-free mixture in this way was more troublesome than by the first method.

In addition to employing a gas free from oxygen, it was considered interesting to examine the synthesis at arc temperature under such conditions that the same volume of nitrogen and hydrogen was repassed a number of times through the arc, the ammonia formed at each passage being absorbed and measured. It is obvious that any trace of oxygen would, particularly by reason of the hydrogen present, be removed during the first few passages through the arc, and that the conversion to ammonia of an approximately constant percentage of the gas-mixture during

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each successive passage would confirm beyond doubt the direct nature of the synthesis.

The experimental method employed consisted in confining a known volume of an oxygen-free mixture of nitrogen and hydrogen in a graduated vertical glass capillary tube about 1 metre long. The upper end of this tube was fused on to a second, short, horizontal capillary tube containing platinum wire electrodes 0·5 mm. apart, between which a small induction arc, as described in a previous communication, could be formed, this second capillary tube ending in a small absorption pipette filled with dilute sulphuric acid. The lower end of the graduated capillary tube was sealed by means of mercury covered with a small quantity of sulphuric acid, and, by the regulated motion of this seal up and down the graduated tube, the thread of gas could be passed and repassed through the arc as often as desired. An approximately uniform rate of passage was obtained by making the graduated capillary tube one limb of a U-tube and causing the required motion by means of a mercury flow, this being normally regulated so that each double passage through the arc occupied about six minutes when 1 c.c. of the gas mixture was taken for experiment.

Working as above described, the ammonia formed during each upward passage was removed by the small absorption pipette sealed to the other end of the short capillary arc tube, whilst that produced during each downward passage was absorbed by sulphuric acid clinging to the side of the graduated capillary. The arc tube was, of course, not allowed to become wet on account of the danger of fracture, and the thread of gas, after its introduction, passed no joints by means of which penetration of air might occur.

Table II summarises the results obtained in two experiments of this nature, the estimation of ammonia being in this case carried out volumetrically by noting the contraction after each passage. A preliminary small expansion occurred on starting the arc, and passage was only begun after the volume had become more or less constant.

The yields of ammonia are much the same as those previously found for such arcs by other methods of analysis and with more accurate control over the rate of passage. Probably, by reason of the more rapid nature of the cooling, the yields are slightly higher than those obtained with the larger arc described in the first part of the present paper. Each cm. of the graduated capillary corresponded with 0·01 c.c. of gas, so that the volume could be read off with fair accuracy to 0·001 c.c.

TABLE II.

No. of expt.	Vol. of gas passed through arc. c.c.	No. of passages since beginning of expt.	Contraction after double passage through arc. c.c.	Percentage of ammonia formed.
1	0·74 (original volume)	2	0·025	1·7
	0·715	4	0·025	1·7
	0·69	6	0·02	1·5
	0·67	8	0·025	1·9
	0·645	10	0·018	1·4
	0·627	12	0·022	1·8
	0·605	14	0·015	1·2
	0·59	16	0·02	1·7
	0·825 (original volume)	2	0·03	1·8
	0·795	4	0·025	1·6
	0·77	6	0·02	1·3
	0·75	8	0·027	1·8
	0·723	10	0·023	1·6
	0·70	12	0·02	1·4
	0·68	14	0·025	1·8
	0·655	16	0·025	1·9
	0·63	18	0·025	2·0
	0·605	20	0·01	0·8
	0·595	22	0·02	1·7
	0·575	24	0·02	1·7
	0·555	26	0·023	2·0
	0·532	28	0·022	2·0
	0·51	30	0·02	1·9
	0·49	32	0·015	1·5
	0·475	34	0·015	1·6

The experimental conditions, including control of rate of flow and the method of analysis, were not suitable for very accurate measurements, but the approximate constancy of the yield of ammonia, and especially the absence of any indication that a normal amount of ammonia is formed during the first passage and little or none during subsequent passages, appears to demonstrate without doubt the direct nature of the synthesis at high temperatures.

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XIII.—*The Effect of some Simple Electrolytes on the Temperature of Maximum Density of Water.*

By ROBERT WRIGHT.

ROSETTI (*Ann. Chim. Phys.*, 1867, [iv], **10**, 461; 1869, **17**, 370) has given a fairly exhaustive account of the early work carried out

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on the determination of the temperature of maximum density of water and of a few salt solutions. A considerable portion of this work is due to Despretz (*Ann. Chim. Phys.*, 1839, [ii], **70**, 49; 1840, **73**, 296), and the most important result is embodied in the following law named after that investigator: "The lowering of the temperature of the point of maximum density of water caused by the addition of a solute is directly proportional to the concentration of the latter."

An attempt was made by Rosetti to connect the lowering of the temperature of maximum density brought about by the addition of a solute with the lowering of the freezing point produced by the same cause, but it was found impossible to formulate any general law, for although the ratio of the two lowerings was constant for any given solute at different concentrations, still a different ratio was obtained by the use of a second solute. In other words, whilst the lowering of the freezing point—being connected with the osmotic pressure of the solution—depends only on the concentration of the solute molecules, the lowering of the point of maximum density depends on the nature as well as on the number of dissolved molecules.

Coppet, in a series of researches (*Ann. Chim. Phys.*, 1894, [vii], **3**, 246, 268; *Compt. rend.*, 1897, **125**, 533; 1899, **128**, 1559; 1900, **131**, 178; 1901, **132**, 1218; 1902, **134**, 1208), has determined the molecular lowering of the temperature of maximum density for a number of salts of the alkalis, that is, the lowering produced by a gram-molecule of salt per litre, and the following table contains the more important of his results:

TABLE I.

	Chloride.	Bromide.	Iodide
Rubidium	11·7	13·2	15·6
Potassium..............	11·6	12·8	15·4
Sodium	13·2	14·5	17·0
Lithium	6·0	7·0	8·3
Ammonium	7·2	8·7	11·1

From an examination of these figures, Coppet points out that of the three acid radicles, the iodide has the greatest and the chloride the least effect, and as a general conclusion states that: "Le rapport entre les abaissements produit par le chlorure et le bromure (ou le bromure et le iodure) du même métal est sensiblement le même pour tous les métaux du groupe." The ratio varies between the values 0·78 and 0·91.

From the results of the present investigation, carried out with

monobasic inorganic acids and their salts with univalent metals, it will be shown that the lowering produced by any given salt conforms to a simple general rule, and can, in fact, be calculated from the known lowerings produced by other salts. The results of the measurements are given in table II, which contains the figures obtained for solutions varying in strength between semi- and one-sixteenth-molecular, the normal, or molecular lowerings, being calculated from those of lower concentration.

TABLE II.

Lowering of the Temperature of Maximum Density of Salt Solutions.

	$M/16.$	$M/8.$	$M/4.$	$M/2.$	Molecular lowering.
HCl	—	0·7	1·3	2·6	5·2
LiCl	—	—	1·4	2·8	5·6
NaCl	—	1·6	3·1	6·2	12·4
KCl	—	1·4	2·8	5·5	11·0
NH$_4$Cl	—	1·0	1·8	3·6	7·2
HBr	—	0·9	1·8	3·7	7·4
LiBr	—	—	1·9	3·8	7·6
NaBr................	—	1·8	3·7	7·4	14·8
KBr	—	1·6	3·2	6·5	13·0
NH$_4$Br	—	1·2	2·3	4·7	9·4
HI	—	1·2	2·2	——	8·8
LiI....................	—	1·2	2·3	——	9·2
NaI	1·0	2·0	4·0	—	16·4
KI	0·9	1·8	3·7	—	14·8
NH$_4$I................	0·7	1·4	2·7	—	10·8
HNO$_3$	0·8	1·6	3·1	——	12·4
LiNO$_3$	—	1·6	3·1	· ·	12·4
NaNO$_3$	1·3	2·5	5·0	—	20·0
KNO$_3$	1·1	2·2	4·5	——	18·0
NH$_4$NO$_3$	0·9	1·8	3·6	——	14·4

It will be seen at once that the results agree with the law of Despretz, the semi-molecular solutions giving twice the depression of the corresponding fourth-molecular. Further, it is obvious that the lowering is not connected with the osmotic pressure, as the values shown for the molecular lowerings of different solutes vary greatly; nor is a consideration of the difference in the degree of ionisation sufficient to account for this abnormality, since the various solutions of any given concentration are practically ionised to the same extent.

The regularity running through all the measurements can readily be seen if the difference between the lowering shown by any acid and, say, its sodium salt is considered. This difference for the four

acids tabulated has the values $7\cdot2, 7\cdot4, 7\cdot6$, and $7\cdot6$; thus the replacement of the hydrogen ion by sodium causes a practically constant increase in the molecular lowering. A similar increase is found when potassium is used instead of sodium, the average value being $5\cdot75$, whilst for ammonium the value is $2\cdot0$. Further, the same effect is observed in the case of the acid radicle; thus, the replacement of chlorine by bromine increases the molecular lowering by $2\cdot1$, whilst the substitution of iodine for chlorine causes an increase of $3\cdot7$.

From a consideration of these results, it is evident that each acidic or basic radicle has its own effect on the lowering of the point of maximum density, and that the effect produced by a salt is equal to the sum of the lowerings caused by the metallic and acidic radicles. Hence, if we take the molecular lowering of hydrochloric acid—which gave the smallest effect of all the substances examined—as standard, we can obtain the molecular lowering of any salt or acid by the addition of two numbers, one corresponding with the acidic and the other with the basic radicle of the salt. It will at once be seen that there is a close resemblance between the above conclusion and Valson's law of moduli, which states that the density of a normal salt solution is the sum of an acidic and a basic effect, and can, in fact, be calculated by adding to the density of a normal solution of a standard substance—ammonium chloride—two figures or moduli, one characteristic of the acidic and the other of the basic radicle of the salt.

The moduli for the lowering of the point of maximum density are given in table III, and the molecular lowering of any salt can be found by adding to the molecular lowering of hydrochloric acid $(5\cdot2)$ the two moduli corresponding with the given salt. For example, the calculated lowering for potassium nitrate would be $5\cdot2$(hydrochloric acid)$+5\cdot75$(potassium)$+7\cdot2$(nitrate)$=18\cdot15$, the actual value found being $18\cdot0$. Several values for each modulus calculated from different salts are shown in the table, together with the mean value derived from them.

TABLE III.

	Cl.	Br.	I.	NO_3.	Average.			
Li	0·6	0·2	0·4	0·0	0·3			
Na	7·2	7·4	7·6	7·6	7·45			
K	5·8	5·6	6·0	5·6	5·75			
NH_4	2·0	2·0	2·0	2·0	2·0			

	H.	Li.	Na.	K.	NH_4.	Average.
Br	2·2	2·0	2·4	2·0	2·2	2·2
I	3·6	3·6	4·0	3·8	3·6	3·7
NO_3	7·2	6·8	7·6	7·0	7·2	7·2

It should be noted that a similar set of moduli could be calculated from the molecular lowerings given by Coppet, although as a rule his values would not be identical with those tabulated; the results, however, approximate to one another fairly closely considering the difference in the experimental methods employed.

We may next consider the results obtained with the weak monobasic organic acids in comparison with their highly ionised salts. Formic, acetic, and propionic acids, together with their sodium and ammonium salts, have been examined.

TABLE IV.

	$N/8.$	$N/4.$	$N/2.$	$N.$
Formic acid	—	1·7	3·6	7·2
Na salt	1·6	3·2	—	12·8
NH_4 salt	—	1·7	3·6	7·2
Acetic acid	—	1·8	3·7	7·4
Na salt	1·5	3·0	—	12·0
NH_4 salt	—	1·6	3·1	6·2
Propionic acid	—	2·0	4·0	8·0
Na salt	1·5	3·0	—	12·0
NH_4 salt	—	1·7	3·4	6·8

The results do not show the normal change, 7·6, which was obtained with strong acids when the hydrogen atom was replaced by sodium, but the difference between the values for the sodium and ammonium salts is constant in all three cases and is identical with that obtained in the case of the inorganic acids. In other words, the highly ionised salts of organic acids behave in the normal manner, whilst the feebly ionised acids themselves are abnormal.

The dibasic acids, with their acid and neutral salts, are also of interest.

TABLE V.

	$M/16.$	$M/8.$	$M/4.$	$M.$
Sulphuric acid	—	3·0	6·1	24·4
NaH salt..................	2·0	4·0	—	32·0
Na_2 salt	2·0	4·0	—	32·0
Oxalic acid	—	1·5	3·0	12·0
NaH salt..................	—	2·4	—	19·2
Na_2 salt	2·0	4·0	—	32·0
Succinic acid	—	1·7	3·4	13·6
NaH salt..................	—	2·5	—	20·0
Na_2 salt	1·5	2·9	—	23·2

It will be seen that the replacement of one hydrogen atom by

sodium in the two stronger acids gives values approximating to the normal, whilst succinic acid gives a slightly lower value, thus resembling the weak monobasic acetic and propionic acids. In all cases, the replacement of the second hydrogen atom is quite abnormal and differs widely in the three cases. From the normal behaviour of the acid salt, it may be concluded that the ions of sodium hydrogen sulphate consist mainly of $Na^{.}$ and $HSO_4{}'$, and not $H^{.}$ and $NaSO_4{}'$. It should be noticed that as the greatest concentration examined in these acids was $M/4$, the results are not so accurate as with the monobasic acids.

The results obtained for the salts of the bivalent metals show great irregularities, probably on account of the complex ions which are present. For example, the molecular lowering obtained for barium chloride was 24·6 and for barium nitrate 32·8, from which the two values 14·2 and 8·0 are obtained for the modulus of barium. Similar varying results can be obtained from the figures given by Coppet and Müller (*Compt. rend.*, 1902, **34**, 1208) for the lowerings shown by the halogen salts of barium and calcium.

TABLE VI.

	Molecular lowering.		Modulus.
Barium bromide	25·14	26·28	10·9
Barium iodide	29·24	29·42	11·7
Calcium chloride	18·0	18·3	7·8
Calcium bromide	20·12	20·93	5·7
Calcium iodide....................	26·09	26·63	8·7

It will be seen at once that there is no regularity comparable with the case of the univalent metals.

EXPERIMENTAL.

The apparatus employed is shown in the diagram; it consists of a dilatometer with a capacity of about 50 c.c. and fitted with a stem 25 cm. long and of 0·5 mm. bore. To compensate for the change in volume with temperature, a portion of the bulb is filled with mercury; the fraction of the total dilatometer volume thus filled is equal to the ratio between the coefficients of cubical expansion of glass and mercury, so that, on a change of temperature, the expansion or contraction of the metal exactly compensates the expansion or contraction of the bulb, the volume of the latter unoccupied by the mercury thus remaining constant.

The dilatometer is filled by means of a tap funnel and a vacuum

pump. The stem of the dilatometer passes through a rubber cork fitted into the opening of the tap funnel which contains the liquid to be introduced into the dilatometer. The funnel and the attached dilatometer is now inverted and connexion made between it and a filter pump. As the pressure is lowered, the air in the dilatometer bulb bubbles through the liquid in the funnel, and on detaching from the pump, the liquid is forced into the dilatometer by the action of the atmospheric pressure. A second and a third exhaustion are usually necessary, and the last trace of air in the bulb is removed by heating. The dilatometer, with the funnel still attached, is now placed in a vacuum-jacketed vessel filled with brine at about 5°, and allowed to cool. When the apparatus has attained the temperature of the surrounding liquid, it is disconnected from the tap funnel and a few shavings of ice are added to the liquid in the vacuum flask; air is then driven through the cooling mixture, so as to stir it until the ice has melted. The apparatus is now left for a quarter of an hour to allow the dilatometer to assume the temperature of the bath; this temperature is then noted, and the level of the liquid in the dilatometer tube measured; the apparatus is again left, and readings are taken at five-minute intervals until the liquid in the dilatometer ceases to contract; this precaution is necessary in order to ensure that the whole apparatus is in a state of thermal equilibrium. A further small quantity of ice is now added so as to lower the temperature a fraction of a degree, and the process repeated. After several additions of ice, the liquid in the dilatometer reaches its point of maximum density, and on further cooling it expands. As this point is approached, the coefficient of expansion of the liquid diminishes, so that it is difficult to determine the exact temperature of maximum density, and the readings given are only accurate to within about 0·2°.
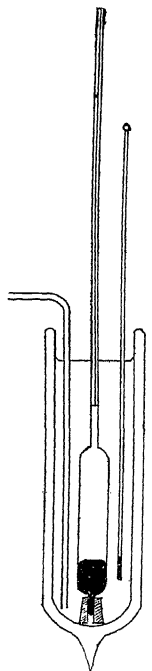
After a measurement, the instrument is warmed so as to expel a little of the contents, and is then inverted so that the mercury runs out. This mercury is dried and reserved for the next determination, whilst the rest of the contents of the dilatometer are removed by means of the filter pump. The instrument is then rinsed with the next liquid to be investigated, and, after the re-

introduction of the mercury, it is filled with the solution and the measurement made as before.

A few other points may be noted. The coefficient of expansion of the glass was calculated between the ordinary temperature and 100° by filling the instrument with mercury and weighing the quantity expelled when heated in a steam-jacket, whilst the volume of the bulb was measured by filling with water and weighing at a known temperature. The stem of the instrument was not graduated, but the level of the liquid below the upper end was determined by means of a depth gauge fitted with a vernier; by this means, a change of level of 0·1 mm. could be detected, and, moreover, the labour of regraduation of the stem after an accident was avoided.

Conclusions.

(1) The lowering of the temperature of the maximum density of water produced by the addition of a solute is directly proportional to the concentration of the latter (law of Despretz).

(2) The lowering produced by a highly ionised binary electrolyte is composed of two separate, independent effects, one due to the acid radicle and the other due to the basic radicle of the electrolyte.

(3) The lowering produced by a highly ionised binary electrolyte of molecular concentration can therefore be calculated by the addition of two moduli to the lowering produced by a molecular solution of a chosen standard substance. The chosen standard was *N*-hydrochloric acid, which gives a lowering of 5·2.

(4) The acid salts of the dibasic acids behave normally, but the neutral salts of such acids and the salts of the bivalent metals do not follow any simple rule in their effect on the temperature of the maximum density.

(5) Feebly ionised organic acids show abnormal effects, but the highly ionised salts derived from them behave in the normal manner.

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XIV.—*Polar and Non-polar Valency.*

By RAJENDRALAL DE.

IN a paper recently published, Briggs (T., 1917, **111**, 267) asks: "What is the valency of cobalt in chloropentammine cobaltic chloride, $\left(Co_{Cl}^{5NH_3}\right)Cl_2$?" This question has suggested the view set forth in the present paper.

From the study of the optical properties of the tetraethylene-diammine-μ-aminonitrodicobaltic salts,

$$en_2 Co \underset{NO_2}{\overset{NH_2}{<\,\,>}} Co\ en_2$$
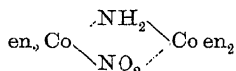
Werner (*Ber.*, 1913, **46**, 3674) concludes that there is no essential difference between the principal and auxiliary valency bonds. Evidently this conclusion may be applicable only to the bonds within the complex radicle (that is, bonds employed in uniting radicles co-ordinated with the cobalt atom). The bonds outside the complex radicle are employed in combining radicles which exist as ions. Their nature is thus entirely different from that of the former ones. A distinction ought therefore to be maintained between the bonds outside the complex radicle and those within it.

We can find an explanation of the valency outside the complex radicle, which is polar in type, from Sir J. J. Thomson's theory of valency. To understand the mechanism of it, let us picture the structure of an atom derived by Thomson. According to him, the atom consists of corpuscles moving in a sphere of uniform positive electrification, and its valency depends on the ease with which corpuscles can escape from, or be received by, the atom. Difficulties, however, arise in explaining the valencies within the complex radicle in the above manner, they being non-polar in type.

During the disintegration of radioactive substances, the negative charges of electricity are carried by β-rays and the positive charges by α-rays. The β-rays consist of expelled particles—not atoms of matter, but free atoms of negative electricity or "electrons." An α-particle, however, consists of two atomic charges of positive electricity combined with a helium atom—a substance inert in the chemical sense. It may therefore be assumed that the positive electricity can have an attraction for the mass itself, even if there be no charge of negative electricity on it. Thomson ("Rays of Positive Electricity and their Application to Chemical Analysis," p. 40) also observes that molecules with positive charges are quite

common, whilst those with negative charges of electricity are very
rare. This property which the positive electricity possesses affords
an explanation of the phenomena of the valencies inside the com-
plex radicle of a complex salt.

In order to explain the phenomena of the above valencies, we
shall consider Rutherford's view as regards the constitution of an
atom. According to him, a positive nucleus is situated in the
centre, whilst electrons move around it in various concentric rings.
We shall conceive this nucleus as having a binding capacity for
the radicles which are co-ordinated with a metallic atom in the
case of complex salts. It is significant that no positive radicles,
such as ammonium, tetramethylammonium, etc., which can exist
as cations, have been observed to combine with a metallic atom
forming a complex radicle. Negative radicles, such as Cl (chloro-),
NO_2 (nitro-), etc., however, do form a complex radicle with a
metallic atom. These negative radicles also carry negative charges
of electricity when they exist as anions.

Let us form a picture of the mechanism as conceived above.
We have the positive nucleus of the metallic atom (capable of
forming a complex radicle) in the centre, and around it there are
various concentric rings along which the electrons move. We may
assume that adjacent to the outermost ring of electrons constituting
the atomic structure there are the neutral molecules, for example,
NH_3, H_2O, etc., or the negative radicles, for example, Cl, NO_2,
etc., or both these neutral and negative radicles, held by the
influence of the positive nucleus of the metallic atom concerned.

Accordingly, in the case of tetraethylenediammine-μ-aminonitro-
dicobaltic salts, radicles within the complex radicle may be sup-
posed to be attached to the positive nuclei of its cobalt atoms, and
thereby, the valencies within the complex radicle being taken to
be all alike, the two cobalt atoms become linked to the two groups
in the middle, namely, NO_2 and NH_2, in a similar way.

The conditions favourable to the formation of complex salts
may now be stated. The number of concentric rings in the struc-
ture of an atom grows large as the atomic weight increases, and,
thereby, the structure also becomes more complex. According to
Rutherford, however (Soddy, "The Chemistry of the Radio-
elements," 1914, Part II, p. 39), the mass of an atom is concen-
trated in an exceedingly small central nucleus. Hence, with the
decrease in the atomic volume, only the rings will decrease in size,
and the outermost ring will approach nearer to the nucleus. We
have already supposed the radicles, co-ordinated with a metallic
atom, to be placed adjacent to its outermost ring of electrons and
also bound by its nucleus. Evidently, the attraction of the nucleus

for the mass of the radicles would increase where there are possibilities of their being placed near to the nucleus, that is to say, where the atomic volume is small. In fact, metals that are capable of forming complex salts, as, for example, chromium, iron, manganese, cobalt, nickel, copper, ruthenium, rhodium, palladium, osmium, iridium, platinum, gold, etc., are situated on the troughs of Lothar Meyer's atomic volume curve. Here it may also be mentioned that Ephraim (*Ber.*, 1912, **45**, 1322; 1913, **46**, 3103; 1914, **47**, 1828; *Zeitsch. physikal. Chem.*, 1913, **81**, 513, 539; **83**, 196), from his study of the strength of the auxiliary valencies of various metals, has drawn the conclusion that the strength of the auxiliary valencies falls with the increase of the atomic volume of the metal concerned. We thus find a further support for the above assumption.

It will be observed that the metals which form complex salts are mostly found both in the "ous" and the "ic" state of their ionic condition, as, for instance, we have $Cr^{..}$ (chromous), $Cr^{...}$ (chromic), $Co^{..}$ (cobaltous), $Co^{...}$ (cobaltic), etc. It may also possibly be that the "ous" condition of the metallic ion is more favourable to the formation of a complex radicle. During the reduction of a metallic ion from the "ic" to the "ous" state, there is an alteration in the electric charge of its rings, and the probability is that this alteration is confined to the outermost ring (Soddy, *ibid.*). Evidently, in the "ous" condition of the metallic atom, there is a less number of electrons in its outermost ring. Keeping in view the structure of an atom, it would be natural to expect that, ordinarily, the outer rings of electrons would offer themselves as a shield against the attraction of the positive nucleus for the radicles which may be co-ordinated with a metallic atom. The case is, however, different in its "ous" state, for, there being produced a weakness in the shield, due to a less number of electrons in the ring, the attraction of the nucleus will obtain an opportunity of manifesting itself by forming a complex radicle. It is known that chromic chloride has to be reduced to the chromous state for the preparation of chrom-ammonia salts (Christensen, *J. pr. Chem.*, 1881, [ii], **23**, 54). Similarly, in the preparation of cobalt—ammonia and platinum—ammonia compounds (Gerhardt, *Annalen*, 1850, **76**, 307), the starting materials are the "ous" salts of the metal concerned.

Lastly, it is found that the formation of a complex anion is a more general phenomenon than the formation of a complex cation; for example, there are compounds of the type $[M(C_2O_4)_3]R_3$, where M may be Vd, Cr, Mn, Fe, Co, Rh, Al, As, Sb, or Bi (Werner, "New Ideas on Inorganic Chemistry," p. 115, ed. 1911). It

seems possible that there is a connexion between the increase of attraction of a metallic atom for these negative radicles (co-ordinated with it) and the cause which occasions the presence of negative charges of electricity on them when they exist as anions.

We have already supposed that the valencies outside the complex radicle are caused by electrons of the outermost ring constituting the atomic structure. These electrons may therefore be termed *valence-electrons*. Obviously, the number of the valence-electrons of a metallic atom corresponds with that of its maximum valencies outside the complex radicle. In the case of the complex metal–ammonia compounds, this maximum valency is exhibited when all the radicles co-ordinated with the metallic atom are NH_3 or H_2O, and when a negative radicle is introduced into the above complex radicle the number of valencies outside the complex one is decreased (that is, the number of valence-electrons appears to become less). We may call those valence-electrons which seem to have vanished in this way *bound valence-electrons*, and those which have caused the appearance of valencies outside the complex radicle *free valence-electrons*. We may also notice that the maximum number of free valence-electrons (that is, electrons which can escape from a metallic atom, forming a complex cation) is the same as the maximum number of electrons which can be received by the atom in addition to its own valence-electrons, when it forms a part of a complex anion. For illustrating this point, we may cite the compounds: (i) $[Co(NH_3)_6]Cl_3$, where the complex radicle is a ter-valent cation, (ii) $K_3[Co(NO_2)_6]$, where the complex radicle is a tervalent anion, and (iii) $[(NH_3)_3Co(NO_2)_3]$, a non-electrolyte. In the third compound, no electron has escaped or been received by the metallic atom, but all the three valence-electrons, along with the three univalent negative radicles, have been bound by its positive nucleus. Regarding the question at hand, namely, that of the number of valencies in chloropentamminecobaltic chloride, it may be said that here the cobalt atom contains three valence-electrons—one is bound along with the univalent chloro-radicle co-ordinated with cobalt, and the remaining two have caused the appearance of valencies of polar type outside the complex radicle. Besides these three valence-electrons, the metallic atom possesses six valency bonds of non-polar type caused by the attraction of its positive nucleus.

The structure of the complex radicle as conceived above explains also the phenomenon of the directional nature of the auxiliary valency bonds, indicated by the stereoisomeric compounds of complex metal–ammonia salts, for the nucleus, being centrally placed in the structure of an atom (metal), has an advantage in exerting

its attraction along different directions, which the electrons moving in their orbits cannot possibly have. The assumption of the nuclear attraction, however, need not be confined to these cases of complex derivatives alone. The phenomena of non-polar valency may, in general, be considered to have arisen from this attraction.

The kind of valency exhibited in organic compounds is a typical non-polar one. If we compare the valencies of the carbon atom with those of metallic ones, employed in co-ordinating radicles with them, we find that both these two kinds are non-polar and directional in nature (shown by the stereoisomerides of the carbon compounds and those of complex metal–ammonia derivatives). This similarity in their character may indicate the probability of their being brought about by the same cause, namely, by the attraction of the positive nucleus of an atom. The assumption receives further support from the small atomic volume of carbon (as shown in Lothar Meyer's atomic volume curve). It has already been supposed that the attraction of the nucleus for radicles should increase as the atomic volume decreases, and this should tend to a maximum when the volume becomes very small.

Nernst is of opinion that the forces by which the carbon atoms in a crystal of diamond are held together are identical with the attraction of its four valencies called into play in the formation of organic compounds, that is to say, "the forces of cohesion are identical in nature with the forces of chemical affinity" ("The Theory of Solid State," p. 6). The cohesive forces are found to increase with the decrease of the atomic volume of elements. They may therefore arise from the very same nuclear attraction of atoms mentioned before. An inspection of the behaviour of carbon and its compounds might help in giving some light in this direction.

In the process of the synthesis of diamond, an immense pressure is brought about by the contraction of iron in which carbon has been dissolved. Evidently, for effecting union (that is, saturation of the valencies of carbon atoms), the atoms are required to be brought very near to one another. It may also be noted that in the case of the carbides of metals, the carbides Li_2C_2, CaC_2, etc., where the metals are of large atomic volumes, are decomposed by water, whilst the carbides Cr_3C_2, Cr_4C, etc., where the metals in combination are placed on a trough in the atomic volume curve (that is, are of small atomic volumes), form stable compounds. Taking into consideration that the mass of an atom is concentrated in an exceedingly small central nucleus in the structure, it seems possible that carbon atoms would exert only a very feeble attraction when placed a little apart or when combined with metals of large atomic volumes. The various rings of electrons around the

nucleus, which have already been compared to shields, may also occasion a further hindrance in their union.

Further light will be thrown on the above if the following view is taken of the constitution of triphenylmethyl. It is found that in solution triphenylmethyl has a molecular weight corresponding with the formula $(CPh_3)_2$ (Gomberg and Cone, *Ber.*, 1904, **37**, 2033). This is what may be expected from its mode of preparation :

$$2CPh_3Br + 2Ag = 2AgBr + CPh_3 \cdot CPh_3.$$
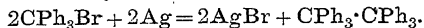
As the compound is very reactive, even at a low temperature, it has been assumed that it is rather a derivative of tervalent carbon. Exposure to the air, even for a very short time, is sufficient to transform it into a peroxide of the constitution $CPh_3 \cdot O \cdot O \cdot CPh_3$.

We may, however, represent the constitution of triphenylmethyl as $CPh_3 \ldots CPh_3$. The weak attraction between the two carbon atoms is shown by the dotted line. The feebleness of their attraction may be due to the inability of the carbon atoms to approach very near to each other on account of the hindrance caused by the large phenyl groups attached to them. The hindrance referred to may be of the type similar to that of steric hindrance (Wegscheider, *Monatsh.*, 1895, **16**, 148), and their reactivity may be due to the possibility of their drawing small atoms very near to them. Viewing the constitution given for the oxidation product, it is seen that by the intervening of two oxygen atoms the large radicles have been placed apart, and by the union of the two carbon atoms with two oxygen atoms (small indeed compared with the triphenylmethyl radicle) a stable compound has been formed.

According to our assumption, radicles bound by the positive nucleus should not show any polar character. Although the valency of carbon is ordinarily non-polar, there are a few organic compounds where it seems to function as polar, as, for instance, in hydrogen cyanide and in organic acids, where we have the radicles $\cdot C \vdots N$ or $\cdot N \vdots C$ and $R \cdot CO_2 \cdot$ respectively, besides hydrion. There are also sodium acetylide, $CH \vdots CNa$, silver acetylide, C_2Ag_2, and cuprous acetylide, C_2Cu_2, where the hydrogen atoms of acetylene have been displaced by metallic atoms. In order to explain this anomaly, we may consider Sir J. J. Thomson's observation that " when the discharge tube contains such gases as CH_4, CO_2, CO, where there are no bonds between two carbon atoms in the molecule, we find negatively charged carbon atoms, but no negatively charged molecules. When, however, we use compounds such as acetylene, $HC \vdots CH$, ethylene, $H_2C \vdots CH_2$, or ethane, $H_3C \cdot CH_3$, where, according to the usual interpretation of the constitution of these substances, there are bonds between carbon atoms in the molecule, then we find molecules as well as atoms of carbon with the negative

charge " (*loc. cit.*). He is also of the opinion that on account of the unsaturated valencies of the carbon atoms in the molecule, it has been possible for the negative corpuscles to become attached to them (*ibid.*). A similar explanation may be applicable in the above cases. In them, more than one bond of carbon has been occupied with the other element combined with it, and a corpuscle received from an adjacent hydrogen atom may become attached to the remaining part of the compound, thus giving rise to their polar character.

Compounds such as LiH, H_2O, NH_3, etc., $Ni(CO)_4$, $Co_2(CO)_8$, etc., and also groups of atoms forming radicles, such as CO_3, NO_3, SO_4, etc., being formed by non-polar valencies, may have their origin in the nuclear attraction. We may also ascribe the forces by which atoms and molecules in a crystal are held together to the same attraction. These forces have been supposed to be caused by residual valency, which has also been assumed to bring about the solution of a substance in a solvent (Baly, "Spectroscopy," 1912, p. 487). The phenomena of solution should necessarily be considered to be due to the same attraction of the nucleus. In these cases, the size of the molecules may account for the feeble character of their binding. Lastly, all catalytic substances which are employed in gaseous reactions may be supposed to owe their catalytic action to the positive nuclei of the atoms in them. Indeed, the study of the dissociation of the hydrogen molecule into atoms, and other similar studies, have convinced Langmuir (*J. Amer. Chem. Soc.*, 1916, **38**, 2221) that prior to the dissociation, absorption of hydrogen by tungsten wire, due to its secondary valency, does take place. We see, therefore, that the nuclear attraction plays a great part in all chemical phenomena.

Regarding the number of valencies of the non-polar type for different elements, it may be noted that carbon (placed in the first trough of Lothar Meyer's atomic volume curve) has four valencies, whilst other elements (placed in subsequent troughs of the curve) generally have six. In the case of the complex platinum–ammonium salts, however, the derivatives of the platinous salts, for example, $[(NH_3)_4Pt]Cl_2$, tetra-amminoplatinous chloride, show the number of auxiliary (non-polar) valencies to be four, whilst those of the platinic salts, for example, $[(NH_3)_6Pt]Cl_4$, hexa-amminoplatinic chloride, the number is six. The increase of two non-polar valencies in the latter case has been attended with an increase of two polar ones. Also the directions of these valencies, in the former case, lie in a plane, whilst in the latter case there are two additional directions lying in the same line perpendicular to the above plane. Whether and how the electrons constituting

the atomic structure influence the number and directions of the non-polar valencies of different elements awaits further study.

My best thanks are due to Prof. P. C. Rây for his kind help and encouragement.

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XV.—*The Interaction of Stannous and Arsenious Chlorides.*

By REGINALD GRAHAM DURRANT.

THE action of stannous chloride on arsenious oxide dissolved in hydrochloric acid was first noticed by A. Bettendorf (*Sitzungsber. Niederrhein. Ges. Bonn*, 1869, 128 *) two years after his discovery of yellow arsenic [*ibid.*, 1867, 67, and (full paper) *Annalen*, 1867, **144**, 110].

He records the formation of a voluminous, brown precipitate which proved to be arsenic (96—99 per cent.) with traces of non-removable tin. He showed that the rate of precipitation increases with ascending specific gravity of the arsenious solution. By dissolving magnesium ammonium arsenate in acid he made a standard solution and treated this with stannous chloride in varying dilutions of hydrochloric acid. (His figures will be quoted later on.) From these results he showed that the reaction is extremely delicate. It may be utilised for determining arsenic in sulphuric or crude hydrochloric acid. During a distillation with the latter he observed a faint yellow coloration, which disappeared after a few hours. Arsenic was found to be present in this sample of hydrochloric acid, but he was unable to prove that the fading coloration was due to arsenic.

The observation of this yellow coloration has decided me to record a very remarkable yellow precipitate which, in 1914, I exhibited as "yellow arsenic" to the Science Masters' Association in London. The precipitate was quite bright yellow at first, and was always kept in the dark except when shown for short periods. After a year

* I am indebted to Dr. Hatchett Jackson who recently procured me a rescript of this paper from the Bodleian Library.

it had become a dull mustard colour, being still in the original, well-corked flask and surrounded by the original solution (a mixture of arsenious and stannous chlorides in nearly normal hydrochloric acid). Every effort was made to repeat this, but in vain. When filtered off, the precipitate appeared very dull and shrunken on the paper. After washing, it was specially tested for sulphur (since arsenious sulphide is yellow), but no trace of sulphur was found. The presence of arsenic was proved.

On many points I find that my observations have been anticipated by Bettendorf, in particular the possibility of making the reaction a means of differentiating arsenic from antimony.

EXPERIMENTAL.

The Nature of the Arsenic Precipitated.

Arsenic is probably in a colloidal state before it is precipitated, for (i) the precipitate invariably contains a trace of tin salts (chloride as well as tin), and this cannot be removed completely by prolonged washing; (ii) two similar solutions (reactants, $0\cdot44N$- and $3N$-hydrochloric acid) were left corked for two days and remained quite clear. One was then diluted with an equal volume of water. After four days both had deposited arsenic. A third solution at the start was made up to the lower of the above concentrations and remained perfectly clear for twenty-five days.

The appearance of solid arsenic is always preceded by a pale buff tint; from this a buff-brown precipitate falls, and is best observed from such admixtures as yield a very slow deposit. If this deposit, after washing, is immediately shaken with carbon disulphide, arsenic is found to be dissolved. The yield is rather greater if carbon disulphide is shaken violently with the two chloride solutions while they are interacting. On five occasions small, pale particles were observed to rise from the clear disulphide solution during spontaneous evaporation. They moved about rapidly, congregating in the centre of the surface, then darkened, and finally settled on the bottom of the dish in the form of grey arsenic.

Erdmann (*Zeitsch. anorg. Chem.*, 1902, **32**, 453) obtained arsenic soluble in carbon disulphide by reducing arsenious oxide with zinc dust in the presence of the solvent. Very small quantities were obtained by the author in this way.

These results, and those referred to in the Introduction, indicate that the very earliest deposit of arsenic is of the yellow type, but that unless certain unascertained conditions obtain, the yellow variety spontaneously becomes brown or grey.

Nature and Conditions of the Reaction.

The obvious equation is $2AsCl_3 + 3SnCl_2 = 3SnCl_4 + 2As$, and when weights of the reactants, corresponding with this equation, are placed in hydrochloric acid of sufficiently high concentration the action reaches completion in a few hours. With other weights excess of either reactant corresponds with calculation.   The action has been proved to be irreversible, for, if finely divided arsenic is boiled with solutions of stannic chloride in the presence of hydrochloric acid of varying concentration, in no case does the resulting solution give any precipitate with mercuric chloride.

A very careful experiment was made in order to ascertain if the anhydrous chlorides react.

Fresh arsenious chloride was so arranged that on movement of the handle of an air-pump some would drop on to dry, powdered stannous chloride—also under the receiver.   After four days' final drying with phosphoric oxide, the experiment was made.   Beyond the faintest darkening no discoloration occurred.   On exposure to air a distinct brown colour overspread the powder, and when a drop of water was added a heavy crusting of arsenic appeared immediately.

General Method of Estimating the Rate of Progress of Action.

Separate solutions containing known weights of the two chlorides were made up in known concentrations of hydrochloric acid.   Portions of these solutions were evaluated separately by means of standard permanganate.   The results were found to agree with the known concentrations.   All stock flasks were re-tested from time to time.

Small dry flasks were placed in a large thermostat, and into these definite volumes of both chloride solutions were introduced by separate pipettes.

After definite intervals water was added.   The dilution effectively stops the action.   The contents of each flask were then filtered and uniformly washed.   Standard permanganate was used to determine the amounts of stannous and arsenious chlorides remaining in the filtrates and wash-water.

The action of the permanganate may be expressed :

$$\left. \begin{array}{l} 2AsCl_3 + 2O = 2AsOCl_3 \\ 3SnCl_2 + 3O = 3SnOCl_2 \end{array} \right\} .$$
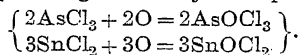
As the filtrates required less permanganate than did the sum of

the separate solutions, the deficit became a measure of the change which had occurred. Two-fifths of this deficit were due to the precipitation of arsenic and the rest to the formation of stannic chloride in the reaction :

$$3SnCl_2 + 2AsCl_3 \longrightarrow 3SnCl_4 + 2As.$$

Errors.—The sources of error in this process are : (1) imperfect washing, (2) loss by adsorption, (3) oxidation of stannous chloride due to access of air.

The two first, considered together, were found to give rise to an error probably less than 2 per cent.

The third source of error was almost eliminated by keeping the stock solutions of stannous chloride in a well-corked flask and by introducing carbon dioxide immediately after use on every occasion. In the same way the reaction took place in small, corked flasks in which the air was displaced by carbon dioxide. Air had access only during the process of filtration.

Calculations.—The recognised integration equations for first and second order reactions were applied to a large number of determinations. In no case did the velocity constants conform to the second order. The results quoted are from the first-order equation, $\frac{1}{t} \log \frac{a}{a-x}$, where $a = 100$, $x =$ percentage of change, and $t =$ time in minutes. Hence the mean value of k for each set of experiments represents a special figure by which the relative speeds may be compared.

TABLE I.

$t = 12 \cdot 5°$. Normalities : $SnCl_2 = 0 \cdot 507$, $AsCl_3 = 0 \cdot 584$, $HCl = 6 \cdot 06$.

$N/4$-Permanganate used. Complete oxidation should correspond with a deficit of 45·6 c.c.

Interval, minutes.	Deficit, c.c.	Percentage change.	$k \times 10^2$.
2	3·65	8·0	1·81
5	9·3	20·8	2·03
8	16·65	36·5	2·46
10	17·05	[37·4]	[2·03]
12	26·25	57·5	3·09
15	29·4	64·5	3·00
20	33·85	74·2	2·94
30	38·45	84·3	2·68
40	40·1	87·9	2·29
50	40·8	89·5	2·96
65	41·9	91·9	[1·68]
100	42·85	93·9	2·21
120	43·6	95·6	2·97
180	43·9	96·3	2·40

Mean   2·57

Various further unimolecular values of k were obtained. These were found to depend more on the concentration of hydrochloric acid than on anything else. The results made it possible to choose suitable concentrations for systematic study.

Influence of Hydrochloric Acid.

In the following experiments 0·2500 gram of stannous chloride

Relative velocities.

Relative velocities of the reaction: $3SnCl_2 + 2AsCl_3 = 3SnCl_4 + 2As$, due to alterations of hydrochloric concentration. See Table II.
$Temperature = 12°.$
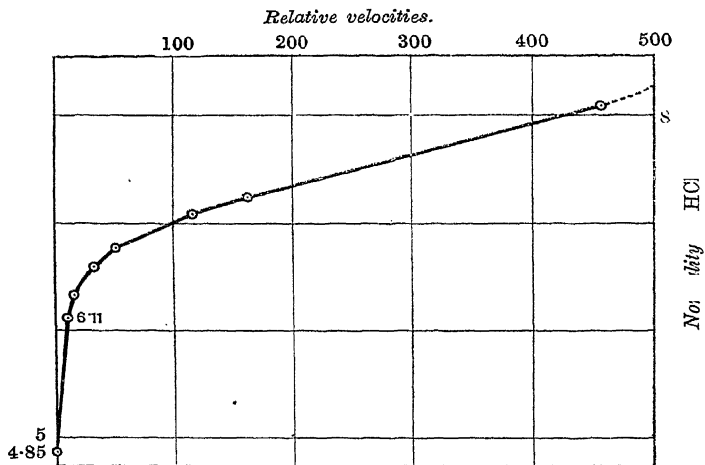
acted on the equivalent weight of arsenious chloride in each case. The concentration of hydrochloric acid alone was varied.

TABLE II.

$t = 12°.$ Reactant Normality $= 0·298.$

Normality of HCl.	Range of change, per cent.	Mean value, $k \times 10^2$.
10·09	40—61	21·2
8·10	36—64	13·5
7·25	32—63	4·76
7·09	34—78	3·43
6·77	13—63	1·46
6·60	21—69	0·944
6·34	26—64	0·436
6·11	41—53	0·293
4·85	19—53	0·0293

The curve, obtained by plotting these relative velocities against concentration of hydrochloric acid between $4·85N$ and $8·10N$, is exceedingly regular. Its sharpest curvature is in the neighbourhood of $6·5N$. If the regularity persisted up to the limit of possible hydrochloric acid concentration (about $10·3N$) then the velocity at $10·09N$ would be well over a thousand times what it is at $4·85N$—as measured it is only 723 times as great.

Influence of Simultaneous Change in Concentration of Reactants.

In all these experiments, the concentration of hydrochloric acid remained constant at $6N$. $t=18·4$.

Four 250 c.c. flasks—A, B, A_1, B_1—contained, respectively, $SnCl_2 = 1·74N$, $AsCl_3 = 1·76N$, $SnCl_2 = 0·87N$, $AsCl_3 = 0·88N$.

The concentration of hydrochloric acid became $6N$ as soon as the mark in each flask was reached.

Equal volumes from A and B were mixed in six small flasks, and after 4, 6, 8, 10, 12, and 14 minutes, respectively, their filtrates were titrated with $N/4$-permanganate.

In the same way, equal volumes from A_1 and B_1 were treated from seven flasks after 24, 32, 48, 64, 80, 96, and 112 minutes, respectively, the filtrates being titrated with $N/8$-permanganate.

In each set, the range of progress was from 30 to 70 per cent.

For AB set, mean value $k \times 10^2 = 4·33$.

For A_1B_1 set, mean value $k_1 \times 10^2 = 0·557$.

Hence $k/k_1 = 7·77$ for the range between 30 and 70 per cent. The range between 30 and 40 per cent., however, gave $k/k_1 = 5·5$.

Effect of altering the Concentration of Each Reactant Separately.

Preliminary work had appeared to show that arsenious chloride reacts as a second, and stannous chloride as a first power.

The following solutions were prepared, tested, and preserved with all possible care. Five c.c. of stannous chloride solution reacted with 5 c.c. of arsenious chloride solution in each case. The washing was strictly uniform, so that errors hence arising were similar.

The mean results, (2) and (4) in the following table, are fairly concordant. Those of (3) and (5) are more so.

The results from comparison of (1), (4), and (5) confirm the preliminary work with respect to arsenious chloride, which is seen to react as a second power.

The period preceding the first appearance of arsenic, from a solution of its chloride at one-fifth the original concentration, was noticed to be just about twenty-five times as great as it had been.

TABLE III.

$$HCl = 6N. \quad t = 16\cdot7^\circ.$$

(1) N-AsCl$_3$ acting on N-SnCl$_2$ in 12 minutes
  required c.c.$N/4$-KMnO$_4$ Required by theory after
                                                    33·3 per cent. change.
        Mean of 2 readings   27·85   26·66
(2) N-AsCl$_3$ on $N/2$-SnCl$_2$ in 12 minutes
        ,,   22·3   23·3
(3) N-AsCl$_3$ on $N/3$-SnCl$_2$ in 12 minutes
        ,,   20·8   22·2
(4) N-SnCl$_2$ on $N/2$-AsCl$_3$ in 48 minutes
        ,,   22·55   23·3
(5) N-SnCl$_2$ on $N/3$-AsCl$_3$ in 108 minutes
        ,,   20·9   22·2

This suggested a method of working to a standard tint, as in Nesslerisation; moreover, the method compares the earlier stages of action on which calculations are more appropriately based.

The tint used in table IV was obtained by the action of hydrogen sulphide on a very dilute solution of lead acetate.

TABLE IV.

$$HCl = 6N. \quad t = 10^\circ.$$

Times to reach Standard Tint are given in Seconds.

Stannous chloride.	Arsenious chloride }	→ N.	→ $N/2$.	→ $N/3$.	Total.	Ratio.	$\sqrt{c}$.
N		30	110	260	400	1·0	1·0
$N/2$		40	160	360	560	1·40	1·41
$N/3$		50	220	460	730	1·82	1·73
Total		120	490	1080			
Ratio		1	4·08	9			
$1/c^2$		1	4	9			

A similar set of nine readings referred to another artificial standard tint gave ratios: powers of AsCl$_3$, $1:4\cdot3:10\cdot0$; powers of SnCl$_2$, $1:1\cdot37:1\cdot80$.

The $N/3$-stannous chloride solution, on testing, was found to have deteriorated slightly; the others had not.

A solution of $N/4$-stannous chloride was made. Using $N/2$-arsenious chloride against $N/2$- and $N/4$-stannous chloride, the times were 230 and 320 seconds respectively, giving a ratio $1/1\cdot39$, again closely approaching $1/\sqrt{2}$.

The results here given lead to the conclusion that in this reaction *arsenious chloride reacts as a second power and stannous chloride reacts to the power of the square root of its concentration.*

The figure 5·5, noted in the last paragraph for the change between 30 and 40 per cent., is quite consistent with the results here given, since $2^2 \times \sqrt{2} = 5·64$.

The action of stannous chloride to the square root of its concentration is also in agreement with Bettendorf's figures (*loc. cit.,* 1869). He took 0·001 gram of arsenic dissolved in 1 c.c. in each of five experiments, adding this to a definite amount of stannous chloride solution in the presence of hydrochloric acid. In the four last experiments he also added 50, 100, 200, and 400 c.c. of hydrochloric acid (presumably of similar concentration).

An immediate precipitate occurred in the first experiment, and the arsenic appeared in 5, 8, 12, and 20 minutes, respectively, in the others.

Neglecting 1 c.c. of arsenious chloride + an unknown volume of stannous chloride solution originally taken, his concentrations were $1:2:4:8$, his times were $1:1·6:2·4:4$, figures which approach $1:1·41:2:2·83$, but exceed them in each case, because of the influence of the second power action of arsenious chloride, present in very small relative amount. (His experiments were made to show the delicacy as regards arsenic.)

Effect of Dilution with Water.

The stock solutions, when mixed, were at concentrations $HCl = 6N$ and reactants each at $0·88N$. When undiluted, this mixture produced 70 per cent. change in twelve minutes. The dilutions (in ten steps) finally brought all the concentrations to one-third of the above.

The hydrochloric acid normalities, and the state of change after five days are noted in each case. $t = 16°$. $6N$, $5·45N$, and $5N$ had reached complete change. $4·61N$ 89 per cent., $4·29N$ 59 per cent., $4N$ 24·4 per cent., $3·75N$ 14·2 per cent., $3·53N$ 5·6 per cent., $3·3N$ 3 per cent., $3N$ 1 per cent., and $2N$ no change and no subsequent sign of action after 29 days. This retarding action was made use of in all previous experiments when titrations with permanganate were made, the dilution with water being sufficient to reduce the concentration to one-third or less.

Summary.

(1) There is evidence that arsenic in process of precipitation is partly soluble in carbon disulphide. In certain circumstances, arsenic may appear as a yellow deposit.

(2) The anhydrous chlorides (arsenious and stannous) do not interact.

(3) Acceleration of the action is caused chiefly by increase in the concentration of hydrochloric acid, next by that of arsenious chloride, and least of all by that of stannous chloride. Arsenious chloride acts as a second power and stannous chloride to the power of the square root of its concentration.

Conclusions.

The various phenomena and the figures given can be accounted for on the hypothesis that this action is between chloride ions, arsenious ions, and the stannous complex H_2SnCl_4.

Stoppage by dilution must be due to the destruction of arsenious ions by hydrolytic action.

(1) Chloride ions proceed partly from arsenious chloride and partly from hydrochloric acid, and they act as a first power.

The velocity constants found in table II are thus explained.

HCl normality.	$k \times 10^2$.		k/k.	Cl'/Cl'.
10·09	21·2	......	1·57	7·09
8·10	13·5	......	2·83	3·55
7·25	4·76	......	1·37	1·54
7·09	3·43	......	2·35	2·08
6·77	1·46	......	1·54	1·58
6·60	0·944	......	2·16	1·88
6·34	0·436	......	3·22	2·66
6·11	0·293	......	10·00	5·28
4·85	0·0293	......		
	Aggregate	25·04		25·66

In the last column, the numerator gives the sum of chloride ions due to arsenious chloride and those due to increased hydrochloric acid concentration; the denominator is constant, and represents the chloride ions due to the $0·298N$-arsenious chloride, which is constant throughout the table. In the lower portion of the table, the arsenious chloride is not wholly ionised; in the upper portion, hydrochloric acid becomes less ionised at its higher concentrations. As is seen, *the aggregate acceleration is directly proportional to the increase of chloride concentration*.

(2) Positively charged arsenious ions also act as a first power. Arsenious chloride as a whole appears, therefore, to act as a second power.

(3) That a compound of hydrochloric acid and stannous chloride exists in solution was indicated by Young (*J. Amer. Chem. Soc.*, 1901, **23**, 21, 450), and several stannochlorides, corresponding with

the formula M_2SnCl_4, have recently been described (compare Druce, *Chem. News*, 1918, **117**, 193).   In the reaction, this complex must be decomposed in order to produce stannic chloride, and this decomposition may account for the complex acting to the power of the square root of its concentration.

According to accepted theory, the order of a reaction is governed by the slowest reactant.   The order here is unimolecular, and the slowest reactant is this complex.   Essentially the action consists in the disintegration of the complex by circumambient ions.

THE COLLEGE,
    MARLBOROUGH.   [*Received, July* 30*th,* 1918.]

XVI.—*Experiments on the Elimination of the Carbethoxyl Group from Tautomeric Systems.   Part I.   Derivatives of Indene.*

By CHRISTOPHER KELK INGOLD and JOCELYN FIELD THORPE.

THERE have been placed on record within recent years (T., 1905, **87**, 1669, 1685; 1911, **99**, 2187, and subsequent papers of the same series) a number of experiments dealing with substances possessing the kind of tautomerism which is associated with the three-carbon system

$$CH \cdot C:C.$$

These experiments have for the most part dealt with glutaconic acid and its alkyl derivatives, and the conclusion was reached that glutaconic acid itself has the symmetrical or "normal" structure (II), the unsaturated or "labile" form (I) being too unstable to have any but a momentary existence.

$$CO_2H \cdot CH_2 \cdot CH:CH \cdot CO_2H \qquad CO_2H \cdot \overset{|}{C}H \cdot CH_2 \cdot \overset{|}{C}H \cdot CO_2H .$$
$$\text{(I.)} \qquad\qquad\qquad \text{(II.)}$$
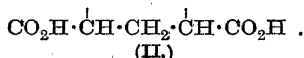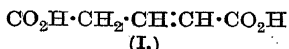
When, however, alkyl groups were introduced into the three-carbon system, the unsaturated form was found to become very noticeably more stable with increasing weight of the substituents.

It was thought desirable to extend these investigations to substances possessing the three-carbon tautomeric complex, but containing groups other than carboxyl attached to its terminal carbon atoms—preferably to some substance in which the possible

symmetry of the molecule could be tested without in any way tampering with the three-carbon system.

Such a substance presents itself in the hydrocarbon indene, the analogy of which to glutaconic acid becomes apparent when the formulæ are written together, thus:

$$CO_2H \cdot CH_2 \atop CO_2H \cdot CH \!\!\!>\!\!CH \qquad \bigcirc {CH_2 \atop CH} \!\!\!>\!\!CH \qquad CO_2H \cdot \overset{|}{C}H \atop CO_2H \cdot \underset{|}{C}H \!\!\!>\!\!CH_2 \qquad \bigcirc {\overset{|}{C}H \atop \underset{|}{C}H} \!\!\!>\!\!CH_2$$

$$(\text{I.}) \qquad\qquad (\text{III.}) \qquad\qquad (\text{II.}) \qquad\qquad (\text{IV.})$$
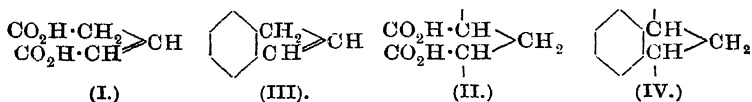
It was hoped originally that the accuracy either of III or of IV might be proved by preparing solid substituted indenes from α-hydrindones of the types V and VI.

$$\bigcirc {CH_2 \atop CO} \!\!\!>\!\!CH_2 \qquad\qquad X\!\!\bigcirc {CH_2 \atop CO} \!\!\!>\!\!CH_2$$

$$(\text{V.}) \qquad\qquad\qquad (\text{VI.})$$

If the unsubstituted three-carbon system of the indene nucleus is symmetrical, as would be expected from analogy to unsubstituted glutaconic acid, the ketones V and VI should yield the same indene, whilst, if unsymmetrical, two different indenes should result.

We have not yet been able to elaborate methods leading to the preparation of suitable ketones of the types V and VI in sufficiently large quantities to ensure the success of this method of attack. In the meantime, however, we have made use of more easily available materials to obtain evidence bearing on the subject, and in particular to investigate a reaction which has been repeatedly observed among esters of the glutaconic series, and appears to be peculiar to tautomeric compounds.

In 1905 the observation was made (Rogerson and Thorpe, T., 1905, **87**, 1702) that ethyl γ-cyano-αβγ-trimethylglutaconate readily passed into ethyl carbonate and ethyl γ-cyano-αβγ-trimethylcrotonate under the influence of cold sodium ethoxide:

$$CO_2Et \cdot CMe(CN) \cdot CMe\!:\!CMe \cdot CO_2Et + EtOH \longrightarrow$$
$$CHMe(CN) \cdot CMe\!:\!CMe \cdot CO_2Et + CO(OEt)_2.$$
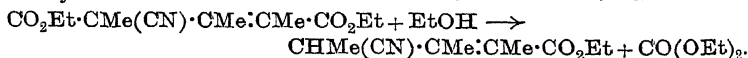
Since that time, fairly extensive use has been made of this reaction in the preparation of a series of alkylated glutaconic esters (Thole and Thorpe, T., 1911, **99**, 2187). Thus the monoalkylated products derived from Conrad and Guthzeit's yellow sodium compound (*Annalen*, 1883, **222**, 259) yielded ethyl carbonate along with tribasic esters:

$$(CO_2Et)_2CR \cdot CH\!:\!C(CO_2Et)_2 + EtOH \longrightarrow$$
$$CO_2Et \cdot CHR \cdot CH\!:\!C(CO_2Et)_2 + CO(OEt)_2.$$
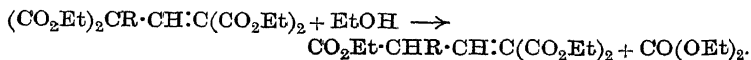
The tribasic esters did not decompose when treated with excess of the same reagent, but on further alkylation gave $\alpha\gamma$-dialkyl derivatives, which reacted readily to form ethyl carbonate and dialkylated glutaconic esters:

$$CO_2Et \cdot CR\!:\!CH \cdot CR'(CO_2Et)_2 + EtOH \longrightarrow$$
$$CO_2Et \cdot CR\!:\!CH \cdot CHR' \cdot CO_2Et + CO(OEt)_2.$$
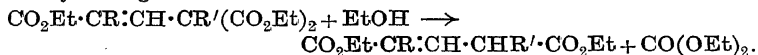
The study of these and similar cases led to a generalisation regarding the determining cause of these reactions. They have always been found to be peculiar, in substances of the glutaconic type, to those in which all the terminal hydrogen atoms of the three-carbon system have been substituted. It was therefore inferred that the tendency in such cases to acquire the hydrogen atom necessary to enable the substance to pass into its tautomeric form is such that a carbethoxyl group readily becomes detached from the molecule and replaced by an atom of hydrogen under the influence of a suitable reagent. We shall have occasion more than once to make use of this general rule.

The ethyl carbonate reaction is therefore very closely bound up with the tautomerism of the three-carbon system. One would not therefore expect derivatives of vinylacetic acid, such as those represented by formulæ VII and VIII, in which the double bond would be purely static, to exhibit this reaction to any marked degree.

Bz·CH	CH₂	(1)ĊH.·ĊH(2)
ĊH	Ph·Ċ	Ċ₆H₄—Ċ(3)
ĊR(CN)·CO₂Et	ĊR(CN)·CO₂Et	(4)ĊR(CN)·COEt
(VII.)	(VIII.)	(IX.)
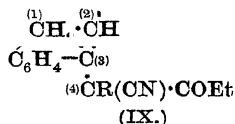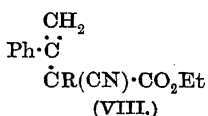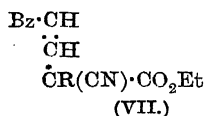
It was therefore decided to prepare an ester of the type IX and investigate its behaviour towards cold sodium ethoxide. The similarity with VII and VIII is clear. If the double bond in the ester IX really possesses the same stable character, we should for similar reasons expect it to be unreactive. This conclusion is in agreement with the generalisation above cited; for if the three-carbon system (1), (2), (3) (see formula IX) in the indene ring is non-tautomeric and the double bond quite static between the carbon atoms (2) and (3), then, since this same double bond enters also into the three-carbon system (2), (3), (4), the latter must be non-tautomeric as well. Its normal form would clearly be incapable of existence, since the central carbon atom (3) is rendered permanently quaternary by the double bond. In such an ester we should not, in view of the above-mentioned generalisation, expect to find any tendency to acquire an atom of hydrogen, which,

if it were acquired, could not possibly be mobile. If, on the contrary, we found that an ester of the type IX actually did possess a noteworthy tendency to acquire a hydrogen atom in place of its carbethoxyl group, we should have to look on the fact as evidence of the tautomeric or dynamic character of the three-carbon system (1), (2), (3) of the indene ring. This follows by simply reversing the argument.

Actually, we have succeeded in preparing a number of indenyl 3-cyanoacetic esters of the type IX, and have found that the lower members of the series possess a very marked tendency to lose their carbethoxyl group as ethyl carbonate when treated with quite a small quantity of sodium ethoxide at 30°. The ester in which $R = Me$, for example, when treated with as little as one-sixth of a molecule of sodium ethoxide, reacts at 30° in the course of a few minutes. The yield of the decarbethoxylated nitrile is 60 per cent., the remainder of the material passing into an insoluble substance of high molecular weight. In all the cases of this reaction investigated, there was a greater or less quantity of insoluble by-product formed along with the nitrile X and ethyl carbonate.

$$\langle\text{indene}\rangle \begin{matrix} CH_2 \\ C \\ CR(CN) \cdot CO_2Et \end{matrix} \!\!> CH \qquad + EtOH \qquad \langle\text{indene}\rangle \begin{matrix} CH_2 \\ C \\ CHR \cdot CN \\ (X.) \end{matrix} \!\!> CH \qquad + CO(OEt)_2.$$
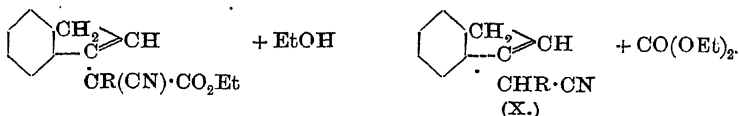
With homologous alkyl derivatives ($R = Et$ and $R = Pr^a$), the reaction becomes successively more sluggish, and an increased quantity of by-product is formed, the yield of nitrile consequently diminishing. This is quite analogous to all that has been observed in regard to the same reaction when applied to the glutaconic esters (T., 1911, **99**, 2192). Two points, to which no analogy has as yet been investigated or observed among the glutaconic esters, require, however, special notice. The ester for which $R = $ allyl was found to be very much more reactive than the corresponding n-propyl derivative. Its reactivity was quite of a similar order to that of the methylated ester. The other point is that a branched chain in the alkyl group appears to inhibit the reaction practically altogether. Thus the esters for which R was *iso*propyl, *iso*butyl, and *iso*amyl gave no nitrile after remaining for twenty-four hours with one-sixth of a molecular proportion of sodium ethoxide at 30°.

In order to obtain a comparative check on these results, we decided to investigate an indenyl-2-cyanoacetic ester of the type XI. This clearly differs from IX only in the fact that in XI the

cyanoacetic residue is attached to the central carbon atom of the indene system. Now if the double bond in XI is entirely static as regards possible interchange across the system (1), (2), (3), then the carbon atom (4) will be the terminal carbon atom of one three-carbon system only, namely, the system (3), (2), (4).

| (XI.) | (XII.) |
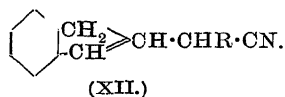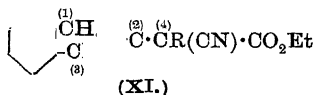
It should therefore differ but little in reactivity from the carbon atom (4) in the corresponding ester of type IX. If, on the other hand, the system (1), (2), (3) of XI possesses a mobile hydrogen atom and a mobile double bond, it is clear that a hydrogen atom attached to the carbon atom (4) will have a double possibility of "wandering"; it might wander either to (1) or to (3). We might, therefore, in view of the general rule, expect to find an ester of the type XI even more prone than the corresponding ester of the type IX to exchange its carbethoxyl group for an atom of hydrogen.

Experiment shows the latter supposition to be amply justified. The ester prepared was that for which $R = Me$. With one-twentieth molecular proportion of sodium ethoxide, there was obtained after three minutes at 15° a practically quantitative yield of the corresponding nitrile (XII: $R = Me$).

This connexion between the ease of elimination of the carbethoxyl group and the potential mobility of the hydrogen attached to the carbon of the cyanoacetic residue suggests a possible explanation of the broad facts both in the indene and glutaconic series in regard to the effect of the size of an alkyl group on the ease of the reaction. It seems likely to be connected with the fact that when heavier alkyl groups were introduced into the glutaconic molecule, they were found to increase the stability of the unsaturated form, and consequently to reduce the predominance of the normal and the potential mobility of the tautomeric hydrogen atom (since tautomerism depends on the possibility of the existence of the normal form). An ester in which the degree of tautomerism of the three-carbon system has been so reduced by the entrance of a large alkyl group would, in view of the generalisation, be expected to exhibit a smaller tendency to acquire an atom of hydrogen, and this is what is actually found to be the case.

In complete accord with the great ease with which the ester XI exchanges its carbethoxyl group for an atom of hydrogen, and with the presumed excessive mobility of the latter, is the behaviour of the unmethylated ester XIV. The esters IX and XI were

obtained by alkylating the esters XIII and XIV respectively.
These esters differ in acidity in the sense that, as one would expect
from the different reactivities of their alkyl derivatives, the cyano-
acetic hydrogen atom of indenyl-2-cyanocetic ester (XIV) is more
loosely attached than that of the corresponding indenyl-3-deriv-
ative (XIII). Thus ethyl indenyl-2-cyanoacetate is a weak acid

(XIII.)   (XIV.)
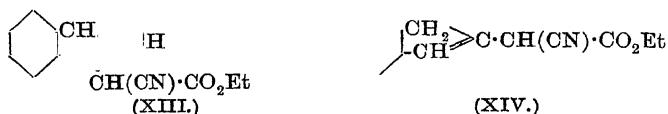
forming a sodium salt which is not hydrolysed in aqueous solution,
being decomposed only by slightly acid substances, such as carbonic
acid. Ethyl indenyl-3-cyanoacetate, on the other hand, only forms
a sodium salt in complete absence of water.

It is perhaps worth noticing that when either of the indenyl-
cyanoacetic esters (XIII and XIV) are converted into or liberated
from their salts, a deep crimson colour is immediately developed.
This fades in the course of a few seconds, both the free esters and
the solid salts being colourless.

Another colour change which was regularly observed in the
course of these experiments took place when the alkylated esters
(IX and XI) were treated with sodium ethoxide. An indigo-blue
colour immediately developed, and gradually faded as the elimina-
tion of the carbethoxyl group proceeded.

The preparation of the indenylcyanoacetic esters (XIII and
XIV) was readily accomplished by condensing α-hydrindone or
β-hydrindone with ethyl cyanoacetate in the presence of piperidine
or diethylamine :
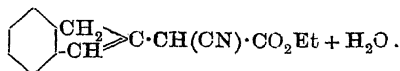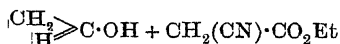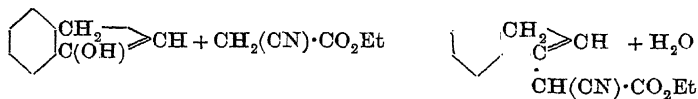
When ethyl indenyl-3-cyanoacetate was hydrolysed either by
acid or by alkali, the cyano-acid (XV) was formed, although not
without considerable decomposition. This acid on heating above
its melting point gave off carbon dioxide, and from the dark-

coloured residue indenyl-3-acetonitrile (XVI) was isolated by

$$
\begin{array}{cc}
\text{CH}_2\!\!>\!\!\text{CH} & \text{CH} \quad \text{H} \\
\quad\!\!-\text{C} & \\
\text{CH(CN)}\cdot\text{CO}_2\text{H} & \text{CH}_2\cdot\text{CN} \\
\text{(XV.)} & \text{(XVI.)}
\end{array}
$$
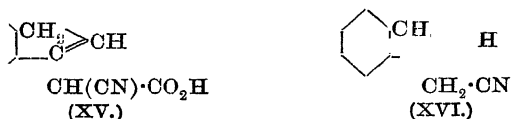
vacuum distillation. This is the first member of the series of homologous nitriles of which X is the type. It cannot, of course, be prepared directly from the cyano-ester (XIII) by the action of sodium ethoxide, for reasons already indicated.

Neither the compound, XVI, nor any of its homologues appears to form a sodium compound when treated with alcoholic sodium ethoxide, and all attempts to introduce another alkyl group into these compounds, using sodium or potassium ethoxide and an alkyl iodide, met with failure. The same was the case when the methylated nitrile, XII, derived from β-hydrindone, was used.

EXPERIMENTAL.

The α-hydrindone required for these experiments was prepared from β-phenylpropionic acid by a method essentially the same as that described by Kipping (T., 1894, **65**, 680), but with the introduction of certain modifications which so improved the yield as to make this substance far more easily available than it has hitherto been.

β-Phenylpropionyl Chloride.—It was found advantageous to use thionyl chloride in the preparation of this substance instead of phosphorus pentachloride. β-Phenylpropionic acid (100 grams) was mixed with an equal weight of thionyl chloride in a flask fitted with an efficient condenser. The reaction was started by gentle heat and allowed to proceed for one and a-half to two hours, when the evolution of gas had ceased. The contents of the flask were then transferred to a Claisen distillation flask and heated at 100°/ 25 mm. until all the thionyl chloride had distilled over. The residue was then fractionated under 22·5 mm. pressure, and 110 grams boiling at 121—122° were collected. The theoretical yield is 112 grams.

α-Hydrindone.—Pure β-phenylpropionyl chloride being thus available, it was found possible to carry out the internal condensation, whereby hydrogen chloride is eliminated and α-hydrindone produced, with much better results than Kipping was able to obtain with the impure chloride at his disposal. Whilst he seldom obtained more than a 56 per yield, it was found that with the pure chloride a yield of 75 per cent. was always secured. The

reaction with the pure chloride is far more violent than with the impure product, and hence the mixture must be heated for a few minutes only. With this exception, the details given by Kipping were closely followed.

β-Hydrindone.—The β-hydrindone required for these experiments was prepared by the improved modification (P., 1911, **27**, 108) of the original process described by Moore and Thorpe (T., 1908, **93**, 165).

Condensation of a-Hydrindone with Ethyl Cyanoacetate in the Presence of Secondary Bases: Ethyl Indenyl-3-cyanoacetate (XIII, p. 148).

Since α-hydrindone readily dissolves in ethyl cyanoacetate, it is not necessary to use any solvent in this condensation. A solution of 19 grams of the ketone in 16 grams of the ester was treated with 6·5 grams of diethylamine and the mixture allowed to remain at 40° for twenty-four hours. At the end of that time, the tube, which contained a stiff paste of crystals of the condensation product, was cooled for an hour at 0°, and the crystals were drained on porous porcelain. The compound separates from alcohol in colourless, needle-shaped crystals melting at 104°; it is moderately soluble in dry ether and readily so in benzene, chloroform, or acetone. The yield represents about 55 per cent. of the theoretical, and is but little affected when piperidine is used in place of diethylamine:

0·1031 gave 0·2805 CO_2 and 0·0538 H_2O.   C=74·20; H=5·80.
0·2492   ,,   13·8 c.c. N_2 at 19° and 742·6 mm.   N=6·19.
   $C_{14}H_{13}O_2N$ requires C=74·0; H=5·7; N=6·2 per cent.

The ester reacts with alcoholic sodium ethoxide, forming a sodium compound, from which the ester is regenerated by the action of water. There is no doubt but that this sodium compound contains the metal attached to the cyanoacetic residue, and that therefore the ester described above has the constitution assigned to it. When alcoholic sodium ethoxide was added to the ester, a deep crimson colour was invariably formed. This faded after a few seconds to a bright yellow, which persisted so long as the solution remained alkaline.

Condensation of a-Hydrindone with Ethyl Cyanoacetate in the Presence of Alcoholic Sodium Ethoxide.

The condensation with sodium ethoxide appears to be of a considerably more complex character than when secondary bases are used. Thus, when an alcoholic solution of α-hydrindone is added

to a hot suspension in alcohol of the sodium compound of ethyl cyanoacetate, there is formed a mixture of substances which may be precipitated by adding water. This mixture consists chiefly of two compounds, melting at 143° and 88—89° respectively, which may be separated and obtained in a state of purity by fractional crystallisation, first from alcohol and finally from a mixture of absolute alcohol and benzene. The former compound was identified with anhydrobis-a-hydrindone (Found: C$=87\cdot74$; H$=5\cdot70$. Calc.: C$=87\cdot8$; H$=5\cdot7$ per cent.), which is recorded as melting at 142—143° (Kipping, T., 1894, **65**, 495).

Ethyl 2 : 3′-*Di-indenyl-3-cyanoacetate,*

$$CH(CN)\cdot CO_2Et$$
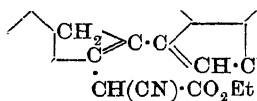
The substance melting at 88—89° may be made to become the principal product if the order in which the condensing substances are mixed is reversed. 3·3 Grams of a-hydrindone were dissolved in a small quantity of hot alcohol, and a hot solution of 0·6 gram of sodium and 2·8 grams of ethyl cyanoacetate in 15 grams of alcohol was slowly added. A few minutes after the addition was complete, the solution was rapidly cooled and poured into water. Hydrochloric acid was then added, and the oily precipitate extracted with ether, the extract washed with dilute sodium carbonate solution and with water, and then dried. The solid residue obtained on evaporation of the ether, when recrystallised from alcohol, weighed 0·8 gram:

0·1545 gave 0·4575 CO_2 and 0·0790 H_2O. C$=80\cdot78$; H$=5\cdot68$.
0·1818 ,, 6·7 c.c. N_2 at 17° and 766·1 mm. N$=4\cdot23$.
    $C_{23}H_{19}O_2N$ requires C$=80\cdot9$; H$=5\cdot6$; N$=4\cdot1$ per cent.

Ethyl 2 : 3′-*di-indenyl-3-cyanoacetate* separates from the usual solvents in pinkish-buff needles melting at 88—89°. It is oxidised instantly by cold alkaline permanganate. With alcoholic sodium ethoxide, it forms a yellow sodium compound, from which the original ester can be regenerated.

Hydrolysis of Ethyl Indenyl-3-cyanoacetate : Indenyl-3-cyanoacetic Acid (XV, p. 149).

The hydrolysis of the ester melting at 104° is a matter of some difficulty, owing to the ease with which it undergoes deep-seated

decomposition with acids and alkalis. Thus, on boiling with acids
(dilute hydrochloric or sulphuric), only a 6 per cent. yield of the
acid is obtained. The acid can be produced in 36 per cent. yield
by alkaline hydrolysis, but only by working within very narrow
limits. Four grams of the ester were treated with 8 c.c. of $4N$-
sodium hydroxide, and the mixture was heated as rapidly as
possible to the boiling point and maintained there for twenty
seconds with vigorous shaking. The oil dissolved, forming a clear
red solution, which was kept boiling for thirty seconds longer and
then rapidly cooled. The crystalline sodium salt which separated
was collected, dissolved in water, and the solution, after passing
through a wet filter, acidified with hydrochloric acid. The acid
separated as a white precipitate, which crystallised from alcohol
in small prisms melting and decomposing at about 200°, the melt-
ing point depending on the rate of heating. The point of instant-
aneous decomposition as measured by the Maquenne block is 237°.
The acid is sparingly soluble in water or dry ether :

0·1251 gave 0·3326 CO_2 and 0·0509 H_2O. C = 72·51 ; H = 4·52.
0·2164   13·8 c.c. N_2 at 19° and 755 mm. N = 7·24.
    $C_{12}H_9O_2N$ requires C = 72·4 ; H = 4·5 ; N = 7·1 per cent.

Indenyl-3-*acetonitrile* (XVI, p. 149).

The pure, recrystallised acid (4·4 grams) was heated at 250° until
the evolution of carbon dioxide had ceased. The dark-coloured
oil which remained was then distilled under diminished pressure
and the colourless distillate cooled in ice. The solid residue, which
melted below the ordinary temperature, was recrystallised from
light petroleum below 0°, and obtained in long, colourless needles
melting at 18° :

0·0820 gave 0·2568 CO_2 and 0·0426 H_2O. C = 85·41 ; H = 5·77.
0·1430   ,,   11·3 c.c. N_2 at 19° and 761·2 mm. N = 9·06.
    $C_{11}H_9N$ requires C = 85·2 ; H = 5·8 ; N = 9·0 per cent.

The attempts which were made to alkylate this nitrile did not
meet with any success, and we were quite unable to find the con-
ditions by which the nitrile could be hydrolysed to the correspond-
ing acid.

*Alkylation of Ethyl Indenyl-3-cyanoacetate and the Elimination
    of the Carbethoxyl Group: Ethyl α-Indenyl-3-α-cyano-
propionate,* $\begin{array}{c}CH_2 \cdot CH \\ | \\ C_6H_4\end{array}\!\!>\!\!C \cdot CMe(CN) \cdot CO_2Et.$
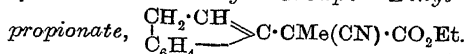
In order to prepare this substance, 12 grams of the ester melt-

ing at 104° were dissolved in the least possible quantity of alcohol at 70° and added to a solution of 1·2 grams of sodium in 16 grams of alcohol. Ten grams of methyl iodide were then added, and the mixture was heated until the yellow colour had entirely disappeared and the solution had become neutral, an operation which usually required ten minutes. The addition of water precipitated an oil which, when extracted by ether, yielded a solid residue after the solvent had been evaporated. The compound crystallises from a mixture of light petroleum and ether in large cubes melting at 60°; it is readily soluble in the usual organic solvents, excepting light petroleum. The yield was 70 per cent. of the theoretical:

0·1418 gave 0·3900 CO_2 and 0·0816 H_2O. C = 74·96; H = 6·39.
0·2818 ,, 14·4 c.c. N_2 at 19° and 783 mm. N = 5·92.
   $C_{15}H_{15}O_2N$ requires C = 74·7; H = 6·2; N = 5·8 per cent.

a-Indenyl-3-propionitrile, $\begin{array}{c}CH_2 \cdot CH \\ C_6H_4 \end{array}\!\!>\!\!C \cdot CHMe \cdot CN.$
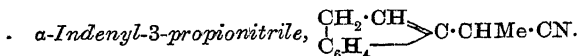
Six grams of the carboxylic ester were dissolved in cold alcohol and an alcoholic solution containing 0·1 gram of sodium was added. The solution was kept at 30° for a short time, when the blue colour which had developed was discharged, and the liquid had a strong odour of ethyl carbonate. The liquid was poured through a filter, water was added, and the precipitate which was formed was induced to solidify by shaking. It was then collected, dried, and extracted with hot light petroleum, the nitrile being deposited from the solvent, on cooling, in long, colourless needles melting at 118°. It may also be recrystallised from dilute alcohol. The yield is 60 per cent. of the theoretical:

0·1032 gave 0·3227 CO_2 and 0·0603 H_2O. C = 85·28; H = 6·49.
0·2118 ,, 15·4 c.c. N_2 at 23° and 771 mm. N = 8·30.
   $C_{12}H_{11}N$ requires C = 85·2; H = 6·5; N = 8·3 per cent.
The nitrile could not be hydrolysed, and all attempts to introduce another alkyl group into it were without success.

Ethyl a-Indenyl-3-a-cyano-n-butyrate,
$\begin{array}{c}CH_2 \cdot CH \\ C_6H_4 \end{array}\!\!>\!\!C \cdot CEt(CN) \cdot CO_2Et.$
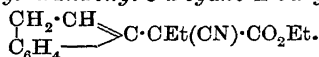
This ester was prepared in the same way as the methyl derivative already described. It is a colourless oil which boils at 200°/25 mm.:

0·1304 gave 0·3604 CO_2 and 0·0785 H_2O. C = 75·38; H = 6·69.
0·2363 ,, 11·6 c.c. N_2 at 22° and 768 mm. N = 5·62.
   $C_{16}H_{17}O_2N$ requires C = 75·3; H = 6·7; N = 5·5 per cent.

α-Indenyl-3-n-butyronitrile, $\begin{matrix} CH_2 \cdot CH \\ C_6H_4 \end{matrix}\!\!>\!\!C \cdot CHEt \cdot CN.$
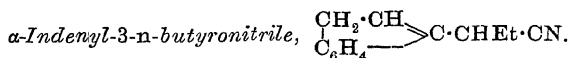
This nitrile was produced from the carboxylic ester by the action of a small quantity of alcoholic sodium ethoxide under the same conditions as those which were described for the methyl derivative. The crude solid precipitated by water was extracted with hot alcohol, and the nitrile obtained from the alcoholic extract by the addition of water. It crystallises from light petroleum in long needles melting at 76°. The yield is 20 per cent. of the theoretical:

0·1306 gave 0·4067 CO_2 and 0·0835 H_2O.   C = 84·93; H = 7·11.
0·1882   ,,   12·6 c.c. N_2 at 23° and 771 mm.   N = 7·64.
   $C_{13}H_{13}N$ requires C = 85·2; H = 7·1; N = 7·7 per cent.

Ethyl α-Indenyl-3-α-cyano-n-valerate,
$\begin{matrix} CH_2 \cdot CH \\ C_6H_4 \end{matrix}\!\!>\!\!C \cdot CPr^a(CN) \cdot CO_2Et.$
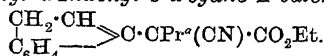
This ester was produced by the action of *n*-propyl iodide on the sodium compound of ethyl indenyl-3-cyanoacetate in alcoholic solution. The reaction was complete after heating for forty-five minutes, and the product was then isolated in the usual way. The ester is an oil which boils at 210°/20 mm.:

0·1259 gave 0·3502 CO_2 and 0·0797 H_2O.   C = 75·86; H = 7·03.
0·2169   ,,   10·0 c.c. N_2 at 22° and 768 mm.   N = 5·26.
   $C_{17}H_{19}O_2N$ requires C = 75·8; H = 7·1; N = 5·2 per cent.

α-Indenyl-3-n-valeronitrile, $\begin{matrix} CH_2 \cdot CH \\ C_6H_4 \end{matrix}\!\!>\!\!C \cdot CHPr^a \cdot CN.$
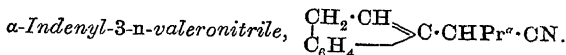
This compound was prepared in the same manner as the ethyl derivative, although in the present instance the reaction proceeded much less readily. It was isolated in the usual way and crystallised from light petroleum in colourless needles melting at 67°. The yield was only 10 per cent. of the theoretical:

0·1028 gave 0·3210 CO_2 and 0·0710 H_2O.   C = 85·16; H = 7·68.
0·2018   ,,   12·8 c.c. N_2 at 23° and 768 mm.   N = 7·20.
   $C_{14}H_{15}N$ requires C = 85·3; H = 7·6; N = 7·1 per cent.

Ethyl α-Indenyl-3-α-cyanoisovalerate,
$\begin{matrix} CH_2 \cdot CH \\ C_6H_4 \end{matrix}\!\!>\!\!C \cdot CPr^\beta(CN) \cdot CO_2Et.$
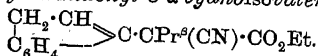
*iso*Propyl iodide was found to react with the sodium compound

of ethyl indenyl-3-cyanoacetate in the same manner as *n*-propyl iodide, and the product was isolated in the same way. In this case, the ester was obtained as a colourless oil which boiled at 260°/120 mm., and solidified in the receiver. The solid crystallised from light petroleum in colourless prisms melting at 72°. The yield represented 60 per cent. of the theoretical:

0·1115 gave 0·3105 CO_2 and 0·0716 H_2O.   C = 75·95; H = 7·15.
0·1859 „   8·6 c.c. N_2 at 22° and 768 mm.   N = 5·28.
$C_{17}H_{19}O_2N$ requires C = 75·8; H = 7·1; N = 5·2 per cent.

This ester was scarcely changed by alcoholic sodium ethoxide under the experimental conditions which caused the other esters to lose their carbethoxyl groups as ethyl carbonate. Most of the original ester and a small amount of insoluble matter were recovered.

Ethyl α-Indenyl-3-α-cyanoallylacetate,
$$\begin{array}{c}CH_2 \cdot CH \\ C_6H_4 \end{array}\!\!\!\!\!\!\!\!> C \cdot C(CH_2 \cdot CH\!:\!CH_2)(CN) \cdot CO_2Et.$$
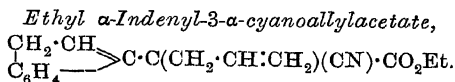
Allyl iodide reacted with the sodium compound of ethyl indenyl-3-cyanoacetate in boiling alcoholic solution in the course of a few seconds. The product was isolated in the usual way and crystallised from light petroleum containing a little dry ether in nearly cubical crystals melting at 65°. The yield was 65 per cent. of the theoretical:

0·1240 gave 0·3484 CO_2 and 0·0715 H_2O.   C = 76·63; H = 6·41.
0·2954 „   13·6 c.c. N_2 at 19° and 764 mm.   N = 5·31.
$C_{17}H_{17}O_2N$ requires C = 76·4; H = 6·4; N = 5·2 per cent.

α-Indenyl-3-*allylacetonitrile,* $\begin{array}{c}CH_2 \cdot CH \\ C_6H_4 \end{array}\!\!\!\!\!\!\!\!> C \cdot CH(CN) \cdot CH_2 \cdot CH_2\!:\!CH_2.$
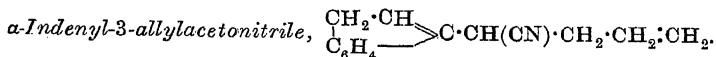
The action of a trace of alcoholic sodium ethoxide on the ester caused the carbethoxyl group to be eliminated, and gave a yield of 40 per cent. of the corresponding nitrile, the same conditions being employed as those described in the former experiments. The nitrile crystallises from light petroleum in colourless needles melting at 108°:

0·1064 gave 0·3366 CO_2 and 0·0647 H_2O.   C = 86·28; H = 6·75.
0·2732 „   17·6 c.c. N_2 at 23° and 768 mm.   N = 7·31.
$C_{14}H_{13}N$ requires C = 86·2; H = 6·7; N = 7·1 per cent.

Ethyl α-Indenyl-3-α-cyanoisohexoate,

$$\begin{array}{c} CH_2 \cdot CH \\ | \\ C_6H_4- \end{array} C \cdot C(CH \cdot CHMe_2)(CN) \cdot CO_2Et.$$
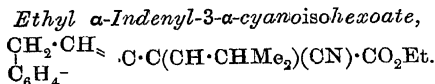
This ester was prepared in the usual manner from *iso*butyl iodide and ethyl indenyl-3-cyanoacetate. It distilled at 260°/40 mm. as a pale yellow oil:

0·1956 gave 0·5481 CO_2 and 0·1290 H_2O.   C = 76·43 ; H = 7·33.
0·2600   ,,   11·6 c.c. N_2 at 22° and 761 mm.   N = 5·07.
    $C_{18}H_{21}O_2N$ requires C = 76·3 ; H = 7·4 ; N = 4·9 per cent.

Like the *iso*propyl derivative, this ester did not lose its carbethoxyl group by treatment with cold sodium ethoxide. After being submitted to the same experimental conditions as the other esters, the recovered material gave, on analysis, C = 76·89, H = 7·56, N = 5·13, indicating that it was practically unchanged. (The de-carbethoxylated compound, $C_{15}H_{17}N$, requires C = 85·3 ; H = 8·1 ; N = 6·6 per cent.)

Ethyl α-Indenyl-3-α-cyanoisoheptoate,

$$\begin{array}{c} CH_2 \cdot CH \\ | \\ C_6H_4- \end{array} \!\!\!\!> C \cdot C(CH_2 \cdot CH_2 \cdot CHMe_2)(CN) \cdot CO_2Et.$$
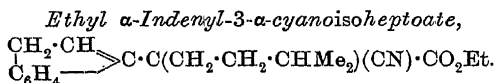
When prepared from the ester melting at 104°, and *iso*amyl iodide, and isolated in the usual way, this ester distilled at 270°/ 34 mm. as an almost colourless oil:

0·1680 gave 0·4749 CO_2 and 0·1173 H_2O.   C = 77·08 ; H = 7·76.
0·2127   ,,   9·0 c.c. N_2 at 22° and 766 mm.   N = 4·80.
    $C_{19}H_{23}O_2N$ requires C = 76·8 ; H = 7·7 ; N = 4·7 per cent.

The carbethoxyl group could not be eliminated under the customary experimental conditions. The material recovered from the solution of sodium ethoxide gave, on analysis, C = 77·31, H = 7·92, N = 4·95, indicating that it consisted of the unchanged compound ($C_{16}H_{19}N$, the carbethoxyl-free compound, requires C = 85·3, H = 8·5, N = 6·2 per cent.).

Condensation of β-Hydrindone with Ethyl Cyanoacetate in the Presence of Secondary Bases.

When a mixture of β-hydrindone and ethyl cyanoacetate is treated with a secondary base such as piperidine or diethylamine, there is generally formed a mixture of two crystalline compounds melting at 116° and 176° respectively. The latter contained no nitrogen and gave, on analysis, C = 87·62, H = 5·81 ($C_{18}H_{14}O$ requires C = 87·8 ; H = 5·7 per cent.). It is therefore probably

identical with anhydrobis-β-hydrindone, the melting point of which is given as approximately 170° (Heusler and Schieffer, *Ber.*, 1899, **32**, 32). The amount of bis-compound formed varies very much with the conditions, and unless the condensation is kept well under control it may become the sole product.

Ethyl Indenyl-2-*cyanoacetate* (XIV, p. 148).

By exercising care, it was found possible to obtain a solid product containing as much as 65 per cent. of ethyl indenyl-2-cyanoacetate and 35 per cent. of anhydrobis-β-hydrindone. Ten grams of β-hydrindone were dissolved in 9 grams of ethyl cyanoacetate, and the solution was cooled below 18° while 30 drops of diethylamine were added. After the addition of each drop, the solution was immediately shaken and well cooled in running water. After completing the addition of the base, the tube containing the mixture was immersed in cold water for thirty minutes, when it was withdrawn and allowed to remain at the ordinary temperature for forty-eight hours. At the end of that time the stiff paste of crystals which filled the tube was spread on porous porcelain and allowed to remain until colourless. The crude solid mixture of condensation products, which usually weighed about 13 grams, was rubbed to a fine powder under a little dry ether and roughly separated by extracting with four times its weight of boiling 95 per cent. alcohol, the bulk of the bis-compound being left undissolved. The crude ester deposited by the filtrate melted between 90° and 110°. It was finely powdered and stirred into an excess of $4N$-sodium hydroxide at 30°, the whole diluted with an equal bulk of water, quickly filtered, and treated with aqueous sodium hydrogen carbonate in excess. The precipitated ester was caused to solidify by shaking, and then collected and triturated with water. After draining and recrystallising from alcohol, it was obtained in long, colourless needles melting at 116°:

0·1261 gave 0·3417 CO_2 and 0·0646 H_2O.   C = 73·91; H = 5·70.
0·1834   ,,   9·7 c.c. N_2 at 16° and 772·5 mm.   N = 6·25.
   $C_{14}H_{13}O_2N$ requires C = 74·0; H = 5·7; N = 6·2 per cent.

The compound is very readily soluble in hot alcohol, but sparingly so in cold. It is also very readily soluble in cold benzene, chloroform, or acetone, and sparingly so in ether or light petroleum. It tends to form coloured products when its alkaline solution is exposed to the air, and the yield obtained by the sodium hydroxide separation therefore depends greatly on the speed with which the operations are carried out.

The separation was also effected by means of a long series of frac-

tional crystallisations from alcohol. The ester obtained by both methods proved to be the same substance, showing that the formation of a sodium salt had not involved any isomeric change, and that the compound must therefore have the structure assigned to it.

The ester is readily soluble in $4N$-sodium hydroxide, and is not reprecipitated when a large bulk of water is added. It is insoluble, however, in sodium carbonate, and is therefore precipitated from the hydroxide solution by carbon dioxide or a bicarbonate. During the precipitation by either of these reagents or by an acid, a transient, red colour always appeared. A similar transient colour was invariably observed when an alcoholic solution of the ester was treated with aqueous or alcoholic potassium hydroxide or alcoholic sodium ethoxide.

Sodium Derivative.—One gram of the ester was dissolved in twice the theoretical quantity of $4N$-sodium hydroxide at 50°. On cooling, a colourless, crystalline sodium derivative separated out. The alkaline liquid was poured off from the crystals, which were then washed with ice-water and dried in a vacuum over phosphoric oxide:

0·3002 gave 0·0860 Na_2SO_4. $Na = 9·28$.

$C_{14}H_{12}O_2NNa$ requires $Na = 9·24$ per cent.

When kept in a closed space, the sodium compound slowly decomposes, acquiring a green colour, but if spread in a thin layer over a large area in a dry atmosphere it can be kept for several weeks. Although the compound itself is colourless, its solution in water is orange. This solution on acidification becomes deep red for a few moments, the colour quickly fading as the free ester separates out.

Methylation of Ethyl Indenyl-2-cyanoacetate and the Elimination of the Carbethoxyl Group: Ethyl α-Indenyl-2-α-cyanopropionate, $C_6H_4 {<}^{CH_2}_{CH}{>} C \cdot CMe(CN) \cdot CO_2Et$.

The methylation of ethyl indenyl-2-cyanoacetate was accomplished both by the action of methyl iodide on the dry sodium compound suspended in alcohol and by the more usual process of treating the free ester with alcoholic sodium ethoxide and methyl iodide. The ester was precipitated with water and extracted with ether. After washing the extract with water and drying, the ether was evaporated and the residual oil crystallised from light petroleum containing a trace of ether. The ester separated in dense, colourless prisms melting at 56°. The yield was about 70 per cent. of the theoretical:

0·1035 gave 0·2837 CO_2 and 0·0580 H_2O.　$C = 74·23$; $H = 6·22$.
0·1653　,,　8·4 c.c. N_2 at 18° and 779 mm.　$N = 5·90$.
　$C_{15}H_{15}O_2N$ requires $C = 74·7$; $H = 6·2$; $N = 5·8$ per cent.

$$\textit{a-Indenyl-2-propionate,}\quad C_6H_4{<}^{CH_2}_{-CH}{>}C\cdot CHMe\cdot CN.$$
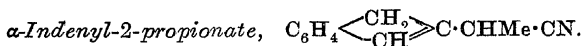
The elimination of the carbethoxyl group of ethyl indenyl-2-cyanopropionate was found to proceed with great ease in the presence of a small quantity of sodium ethoxide. Thus with one-twentieth of a molecular proportion of sodium at 15°, the reaction was complete in about three minutes. On adding water, the nitrile separated out. After allowing the suspension to remain for twenty-four hours, it was filtered, and the solid dried and recrystallised from light petroleum, from which it separated in long, colourless needles melting at 92°:

0·1011 gave 0·3167 CO_2 and 0·0591 H_2O.　$C = 85·43$; $H = 6·49$.
0·1179　,,　8·5 c.c. N_2 at 20° and 764 mm.　$N = 8·22$.
　$C_{12}H_{11}N$ requires $C = 85·2$; $H = 6·5$; $N = 8·3$ per cent.

The yield was practically quantitative.

All attempts to hydrolyse this nitrile resulted in deep-seated decompositions taking place, and we were unable to isolate the corresponding acid. Several attempts also were made to introduce another methyl group into the molecule, but without success.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
　　SOUTH KENSINGTON,　　[Received, December 6th, 1918.]

XVII.—*The Preparation of Monomethylamine from Chloropicrin.*

By PERCY FARADAY FRANKLAND, FREDERICK CHALLENGER, and
NOEL ALBERT NICHOLLS.

THE products of the reduction of chloropicrin seem to vary with the nature of the reducing agent. With stannous chloride and hydrochloric acid, cyanogen chloride is produced (Raschig, *Ber.*, 1885, **18**, 3326). The occasional formation of traces of ammonia was noticed by this chemist, but as a rule, after removing the tin by means of hydrogen sulphide, the product was found to be free from ammonium chloride and the hydrochlorides of hydroxylamine and methylamine. Iron filings and acetic acid (Geisse, *Annalen*, 1859, **109**, 282) or tin and hydrochloric acid (Wallach, *ibid.*, 1877, **184**, 51) give rise to monomethylamine,

$$CCl_3\cdot NO_2 + 12H = CH_3\cdot NH_2 + 3HCl + 2H_2O.$$
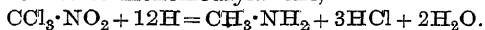
Since chloropicrin may easily be obtained in large quantities, it appeared desirable more closely to investigate its reduction, owing to the importance of monomethylamine in synthetic organic chemistry. It would be inferred from Geisse's paper that the base he obtained was free from ammonia, whilst Wallach states that his product was comparatively very pure and the yield good.

By employing fine iron filings and hydrochloric acid, we have found that the composition of the reduction product depends on the conditions of the experiment. The use of iron and hydrochloric acid in the theoretical quantities (six atomic proportions of iron and nine molecular proportions of acid to one of chloropicrin) in such a way as to prevent the formation of ferrous or ferric hydroxides gave a product rich in ammonium chloride. If chloropicrin is shaken with iron filings and water, the mixture becomes extremely hot and a vigorous reaction sets in, which, however, gradually slackens if no acid is added. By adopting the method employed in the reduction of aromatic nitro-compounds or of nitromethane and nitroethane (Krause, *Chem. Zeit.*, 1916, **40**, 810), the reaction proceeds satisfactorily in the presence of only about one-fortieth of the theoretical amount of hydrochloric acid, and a practically theoretical yield of methylamine hydrochloride is obtained. This usually contains about 4 per cent. of ammonium chloride, but in some of our experiments the quantity of this impurity has been still further reduced. The best results have been obtained by slowly adding the chloropicrin to a well-stirred mixture of iron filings and acidified water. The gradual addition of iron filings to a mixture of acidified water and chloropicrin did not seem to be very satisfactory, so far as could be seen from the few experiments made in this direction. Some reductions carried out by gradually adding chloropicrin to boiling alkaline ferrous hydroxide failed to confirm the results of Geisse (*loc. cit.*), who states that by this method no ammonia is produced. We obtained a product containing about 20 per cent. of ammonium chloride.

The details of a typical large-scale experiment may be briefly outlined. Five hundred grams of fine iron filings were gradually shaken into a large earthenware jar containing 2500 c.c. of water and 60 c.c. of concentrated hydrochloric acid. In this way, the filings were thoroughly moistened and the tendency to clogging was diminished. The jar was fitted with a stirrer and placed in a little cold water; 250 grams of chloropicrin were then gradually added in the course of one-and-a-quarter hours. Too rapid addition of the chloropicrin caused the mixture to froth over. Owing to the large amount of hydrated oxide of iron produced, the stirring was as efficient as possible; otherwise chloropicrin escaped reaction through being enclosed in masses of iron filings or oxide.

The temperature rose considerably, and was maintained at about 50°, when the odour of chloropicrin was found to have disappeared after about three hours. The mixture was then gradually added to a boiling solution of sodium hydroxide contained in a large iron can, into which steam was blown. The methylamine was absorbed in hydrochloric acid, the solution evaporated, and the residue dried at 110° until constant weight was attained. The crude, dry hydrochloride was obtained in this way in a yield of 95·5 per cent., and contained 53·1 per cent. of chlorine, corresponding with an ammonium chloride content of only 3·5 per cent.

That ammonium chloride is actually produced during the reduction of chloropicrin was shown by treating cold concentrated aqueous solutions of the crude hydrochlorides with gaseous hydrogen chloride. The precipitated solid was collected, carefully freed from adhering hydrochloric acid, and analysed, when it was found to be almost pure ammonium chloride. The analyses of the crude methylamine hydrochloride were checked in some instances by an estimation of the platinum in the platinichloride. The hydrochlorides were evaporated with an excess of chloroplatinic acid solution, and the dry residue was extracted with absolute alcohol, whereby only platinum tetrachloride is removed. The possibility of a partial separation of the platinichlorides of the two bases would thus appear to be excluded.

Summary of Results.

Section A.—In the following experiments, the quantity of acid was very small, and the amount of iron theoretically required for the liberation of 12 atomic proportions of hydrogen (supposing sufficient acid had been present) was employed. The temperature was usually allowed to rise to about 50—70°.

Experiment.	1.	2.	3.	4.	5.	6.
Chloropicrin, grams	500	250	250	25	25	25
Iron, grams	1000	500	500	50	50	50
Water, c.c.	3500	2500	2500	200	200	200
Hydrochloric acid, c.c.	100	60	60	12	32 ·	10
Crude hydrochloride, grams	190	98	94	9·5	10·0	9·5
Theoretical weight, grams	205	102·5	102·5	10·2	10·2	10·2
Cl in crude hydrochloride..............	53·3	53·1	53·6	52·9	52·8	53·1
Hence percentage NH_4Cl	5·0	3·5	7·0	2·0	1·5	3·5
Pt in crude platinichloride..............	41·53	41·43	—	—	—	41·33
Hence percentage NH_4Cl	6·5	2·75	—	—	—	1·10

NH_4Cl requires $Cl = 66·5$. $(NH_4)_2PtCl_6$ requires $Pt = 43·96$.

$CH_3 \cdot NH_3Cl$ requires $Cl = 52·6$. $(CH_3 \cdot NH_3)_2PtCl_6$ requires $Pt = 41·36$ per cent.

Section B.—In the experiments described in this section, the quantity of acid employed was much larger (up to 9 molecular proportions, not including the three formed during the reduction), and the iron as in *A.* The chloropicrin and the acid were both added gradually to the iron filings. The percentage of ammonium chloride is seen to have increased considerably.

Experiment.	1.	2.	3.
Chloropicrin, grams............................	25	25	50
Iron, grams	50	50	100
Water, c.c.	100	50	100
Hydrochloric acid, c.c.	200	150	300
Yield of dry hydrochloride, grams	9	6·5	15·0
Theoretical weight, grams	10·2	10·2	20·5
Cl in crude hydrochloride	58·0	60·9	60·5
Hence percentage NH$_4$Cl	40·0	60·0	60·0

Section C.—In these experiments, the chloropicrin was gradually added to a boiling alkaline ferrous sulphate solution. A considerable amount of ammonia was formed.

Experiment I.—Chloropicrin, 25 grams; ferrous sulphate, 550 grams; sodium hydroxide, 300 grams; water, 1800 c.c.

Dry hydrochloride, 7 grams. Theory, 10·2.

Analysis in samples of about 0·2 and 0·1 gram: Cl = 56·0, 55·2. Mean = 55·6, whence NH$_4$Cl = 22 per cent.

Experiment II.—Quantities as in above.

Dry hydrochloride, 9 grams.

Analyses in samples of about 0·5 gram: Cl = 54·8, 54·8, 54·6. Mean = 54·7, whence NH$_4$Cl = 15 per cent.

Interaction of Methylamine and 1 : 2 : 4-*Trinitrobenzene.*

With 1 : 2 : 4-trinitrobenzene, the alcoholic solution of the base gave an almost immediate deposit consisting of yellow needles melting at 175—176°, and at 176° after one crystallisation. The formation of 2 : 4-dinitromethylaniline (m. p. 176—177°) by this method does not seem to have been described.

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XVIII.—*The Alkaloids of* Holarrhena congolensis, *Stapf.*

By FRANK LEE PYMAN.

FRÈRE JUST. GILLET, S.J., a missionary in the Belgian Congo, reported some years ago that, on chewing the leaves of *Holarrhena congolensis*, Stapf, a local anæsthetic effect was produced on the mucous membrane of the mouth. This led the author to examine the alkaloids of the plant in 1913, when a new base, termed *holarrhenine*, $C_{24}H_{38}ON_2$, was isolated, together with the alkaloid conessine, which has been obtained previously by several authors from other species of *Holarrhena*. The physiological action of conessine and holarrhenine was studied by J. H. Burn (*J. Pharmacol.*, 1915, **6**, 305), who found that whilst they had a local anæsthetic action, this property was of no practical value, since they produced local necrosis when injected subcutaneously.

Since it is improbable that the author will continue this investigation, it is desired to put on record the properties of holarrhenine and also the results of a few experiments on conessine carried out at that time. These are for the most part in agreement with the recent work of Giemsa and Halberkann (*Arch. Pharm.*, 1918, **256**, 201), and confirm the formula $C_{24}H_{40}N_2$ supported by these authors, not that—$C_{23}H_{38}N_2$—put forward by Ulrici (*Arch. Pharm.*, 1918, **256**, 57). Giemsa and Halberkann's view, that conessine contains two dialkylamino-groups, is not shared by the present author, who found conessine to contain only three alkyl groups (no doubt methyl groups) attached to the nitrogen atom. Moreover, Polstorff and Schirmer (*Ber.*, 1886, **19**, 84) showed that conessine dimethohydroxide yields, on heating, a crystalline base, together with "ammonia" (doubtless trimethylamine). It is therefore probable that conessine contains an *N*-methyl group forming a link in a heterocyclic ring, to which a side-chain bearing a dimethylaminogroup is attached. Holarrhenine resembles conessine in containing three *N*-alkyl groups. It yields a *monoacetyl* derivative, $C_{26}H_{40}O_2N_2$, which is diacidic, whence it follows that holarrhenine contains a hydroxyl group.

EXPERIMENTAL.

Isolation of the Alkaloids.

Twenty-nine kilograms of the bark of the trunk of *Holarrhena congolensis*, Stapf, were percolated with very dilute hydrochloric

acid. The liquor was made alkaline with ammonia and extracted with chloroform. After distillation of the solvent, the dark, viscous residue was extracted first with light petroleum and then with ether. The light petroleum extract was shaken with dilute hydrochloric acid, the base regenerated with sodium carbonate, and extracted with light petroleum. The extract was distilled, and the residue dissolved in a solution of 0·7 part of hydrated oxalic acid in 4 parts (by weight) of alcohol. On keeping, a colourless, crystalline hydrogen oxalate (m. p. 249°) separated in a yield amounting to 0·9 per cent. of the bark. The oxalate was dissolved in water, the base regenerated by sodium carbonate, and extracted with light petroleum. After distilling the extract, the residue was dissolved in a little acetone and kept, when conessine separated in colourless plates, amounting to 0·25 per cent. of the bark. A further quantity was obtained by working up the mother liquor.

The ethereal extract of the total alkaloids was extracted with dilute hydrochloric acid, and this was basified with ammonia and extracted first with light petroleum and then with ether. The light petroleum extract was worked up as before for conessine. The ethereal extract was concentrated and left for some time, when a small quantity of holarrhenine crystallised out.

Conessine.

The base employed in this investigation was purified by crystallisation from acetone, which is particularly suitable for the purpose, as Giemsa and Halberkann have remarked. The base is only sparingly soluble in cold acetone, but dissolves in boiling acetone to the extent of approximately 10 per cent. On cooling, it separates in large, colourless plates, which apparently contain acetone of crystallisation, for they effloresce quickly in the air, becoming free from solvent. The base melted at 125° (corr.).

Found: $C = 81·0$, $80·7$; $H = 11·3$, $11·4$; $N = 7·9$; Me(attached to N) $= 12·5$, $13·0$.

$C_{24}H_{40}N_2$ requires $C = 80·8$; $H = 11·3$; $N = 7·9$; Me(attached to N) $= 12·6$ per cent.

The molecular weight was determined by the cryoscopic method in benzene:

0·2330 in 29·92 benzene gave $\Delta t = -0·108°$. M.W. $= 361$.
0·4442 ,, 29·92 ,, ,, $\Delta t = -0·213°$. M.W. $= 349$.
$C_{24}H_{40}N_2$ requires M.W. $= 356·5$.

The specific rotatory power of the base was determined in chloroform solution:

$$\alpha_D - 0·28°; \quad c = 7·268; \quad l = 2 \text{ dcm.}; \quad [\alpha]_D - 1·90°.$$

The specific rotatory power of a specimen of the hydrobromide (containing 2·4 per cent. of water) was determined in aqueous solution:

$\alpha_D + 0.56°$; $c = 3.858$; $l = 2$ dcm.; $[\alpha]_D + 7.4°$ for the anhydrous salt.

Conessine hydrogen oxalate forms prisms readily soluble in hot, but rather sparingly so in cold, water, and sparingly soluble in alcohol. It melts and decomposes at 280° (corr.), and is anhydrous.

Found: C = 62·5; H = 8·1.

$C_{24}H_{40}N_2, 2C_2H_2O_4$ (536·5) requires C = 62·6; H = 8·3 per cent.

Holarrhenine, $C_{24}H_{38}ON_2$.

The crude base was first purified by crystallisation from ethyl acetate, when it melted at 190°, and then converted into the hydrobromide. This salt was crystallised from water and washed with acetone. It was then reconverted into the base, and this was recrystallised from ethyl acetate, when it separated in silky needles which melted at 197—198° (corr.). It suffers no loss at 100°. It is insoluble in water, readily soluble in alcohol or chloroform, but sparingly so in cold ethyl acetate, acetone, or ether.

Found: C = 77·5, 77·6, 77·3; H = 10·2, 10·3, 10·7; N = 7·7; Me(attached to N) = 11·1, 12·2.

$C_{24}H_{38}ON_2$ (370·4) requires C = 77·8; H = 10·3; N = 7·6; Me(attached to N) = 12·2 per cent.

The specific rotatory power was determined in chloroform solution:

$$\alpha_D - 0.75°; \quad c = 5.248; \quad l = 2 \text{ dcm.}; \quad [\alpha]_D - 7.1°.$$

The *hydrobromide* crystallises from water in flat needles, which melt at 265—268° (corr.) after drying. It is readily soluble in hot, somewhat sparingly so in cold, water. The air-dried salt contains $3H_2O$ (Found: $H_2O = 9.0$. Calc.: $H_2O = 9.2$ per cent.).

Found, in salt dried at 100°, C = 54·4; H = 8·2; Br = 29·8.

$C_{24}H_{38}ON_2, 2HBr$ (532·3) requires C = 54·1; H = 7·6; Br = 30·0 per cent.

The specific rotatory power was determined in aqueous solution:

$\alpha_D + 1.02°$; $c = 4.630$; $l = 2$ dcm.; $[\alpha]_D + 11.0°$ or $+12.1°$ for the anhydrous salt.

Acetylholarrhenine, prepared by the action of acetic anhydride and anhydrous sodium acetate on holarrhenine, crystallises from acetone in large, colourless, oblong plates which melt at 180° (corr.).

It is insoluble in water, sparingly soluble in cold alcohol, acetone, or ether, but readily so in chloroform.

Found: $C = 75\cdot7$; $H = 9\cdot9$; $N = 6\cdot8$.

Equivalent to HCl, using methyl-orange $= 202$.

$C_{26}H_{40}O_2N_2$ ($412\cdot5$) requires $C = 75\cdot7$; $H = 9\cdot8$; $N = 6\cdot8$ per cent.

XIX.—*Meta-substituted Aromatic Selenium Compounds.*

By FRANK LEE PYMAN.

AT the suggestion of Dr. Charles Walker, of Glasgow, attempts were made, in 1913, to form the selenium analogue of arsanilic acid, namely, *p*-aminophenylselenic acid, $NH_2 \cdot C_6H_4 \cdot SeO_3H$, in order to determine its physiological action. Whilst aniline sulphate and arsenate readily yield sulphanilic acid and arsanilic acid, respectively, at an elevated temperature, no similar compound could be obtained from aniline selenate. It was found, however, that phenylselenious acid gave on nitration a *nitrophenylselenious acid*, which is shown to be the meta-compound in the manner described below. On reducing this compound with sodium hydrogen sulphite, *di*-m-*nitrophenyl diselenide* resulted, and gave *di*-m-*aminophenyl diselenide* on further reduction with sodium sulphide. Di-*m*-aminophenyl diselenide gave on acetylation *di*-m-*acetylaminophenyl diselenide*, from which m-*acetylaminophenylselenious acid* was obtained by oxidation with nitric acid. From this, the salts of m-*acetylaminophenylselenic acid* were obtained on oxidation with potassium permanganate, whilst on attempting to liberate the free acid, hydrolysis took place with the formation of m-*aminophenylselenic acid*:

$$NO_2 \cdot C_6H_4 \cdot SeO_2H \longrightarrow (NO_2 \cdot C_6H_4 \cdot Se)_2 \longrightarrow (NH_2 \cdot C_6H_4 \cdot Se)_2 \longrightarrow$$
$$(NHAc \cdot C_6H_4 \cdot Se)_2 \longrightarrow NHAc \cdot C_6H_4 \cdot SeO_2H \longrightarrow$$
$$NHAc \cdot C_6H_4 \cdot SeO_3K \longrightarrow NH_2 \cdot C_6H_4 \cdot SeO_3H.$$
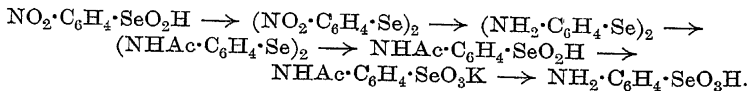
When these results were first communicated to the Society (P., 1914, **30**, 302), the orientation of the nitro-group in nitrophenylselenious acid had not been determined, and in the discussion on the paper, Dr. Tuck suggested that the constitution of this acid might be settled by preparing the three isomerides by the action

of the nitrobenzenediazonium chlorides on potassium selenocyanate and suitable after-treatment. This method had already been applied by Bauer (*Ber.*, 1913, **46**, 92) to the preparation of *o*-nitrophenyl selenocyanate, and by Morgan and Elliot (P., 1914, **30**, 248) to the preparation of *p*-chlorophenyl selenocyanate and their derivatives.

At the author's request, Mr. H. King has now kindly prepared *m*-nitrophenyl selenocyanate, from which he has obtained, on reduction with tin and hydrochloric acid, di-*m*-aminophenyl diselenide, identical with the product resulting from the reduction of nitrophenylselenious acid, thereby proving the constitution of the compounds described above.

Experimental.

Phenylselenious Acid, $PhSeO_2H$.

The preparation of this acid and its nitrate have been described by Stoecker and Krafft (*Ber.*, 1906, **39**, 2197). Diphenyl diselenide (1 part by weight) was dissolved in concentrated nitric acid (40 parts by weight) and heated. On cooling, the well-crystallised nitrate of phenylselenious acid separated. In order to liberate the free acid, the nitrate was dissolved in ammonia and mixed with silver nitrate, when silver phenylselenite was precipitated, and gave the free acid when decomposed with the equivalent quantity of hydrochloric acid.

Doughty (*Amer. Chem. J.*, 1909, **41**, 326) subsequently obtained this acid by the action of hydrochloric acid on phenylselenic acid resulting from the interaction of selenic acid and benzene. He was unable to confirm the previous author's statement that the acid crystallised with $2H_2O$, finding it to be anhydrous.

For the purpose of the present investigation, considerable quantities of this acid were required, and a modification of Stoecker and Krafft's process was adopted. Instead of employing pure diphenyl diselenide, the mixture of this substance with selenophenol, obtained by the action of selenium on magnesium phenyl bromide (Taboury, *Bull. Soc. chim.*, 1903, [iii], **29**, 761), was used. On treating this with 4 c.c.—instead of 30 c.c.—of nitric acid for each gram, phenylselenious acid nitrate was readily prepared in quantity. When mixed with sufficient ammonia to neutralise the nitric acid, it gave free phenylselenious acid, which was found to be practically anhydrous, in agreement with Doughty's observation.

To a solution of magnesium phenyl bromide in dry ether, prepared from 24 grams of magnesium and 157 grams of bromo-

benzene, 79 grams of selenium were added gradually, and the mixture was boiled for half an hour. The product was decomposed with ice and dilute hydrochloric acid, well shaken, and the ethereal layer removed, the aqueous layer being extracted with ether twice again. The ethereal extracts were combined, dried with calcium chloride, and the solvent was removed on the water-bath. The resulting oil (about 130 grams) was then allowed to flow drop by drop into concentrated nitric acid (D 1·4), of which 4 c.c. were employed for each gram of the oil. The nitric acid solution was then digested for an hour on the water-bath and kept, when crude phenylselenious acid nitrate separated in hard crystals. This was collected on asbestos, dissolved in water, and the solution filtered from insoluble matter. The solution was then extracted with ether to remove further impurities, and evaporated to a syrup. On cooling, this set to a chalky mass of the nearly pure nitrate, which, after thorough drying in the air, amounted to about 110 grams. The yield is thus 44 per cent. of the theoretical.

For the preparation of the free acid, 10 grams of the nitrate were dissolved in 20 c.c. of water, and 6 c.c. of 10 per cent. aqueous ammonium hydroxide added. On stirring, phenylselenious acid separated in sandy, yellow grains, which were purified by crystallisation from water. 6·5 Grams of the pure acid were isolated without carrying out the separation to an end, whilst 7·6 grams are required theoretically. Phenylselenious acid, prepared in this way, melted at 124—125° (corr.) after drying at 100°. The air-dried acid was practically anhydrous. (Found, loss at $100° = 0·4$; $C = 37·6$; $H = 3·3$. $C_6H_5 \cdot SeO_2H$ requires $C = 38·0$; $H = 3·2$ per cent.)

Sodium phenylselenite crystallises from water in colourless plates containing $2H_2O$. It is readily soluble in water.

Found, loss at 100°, 14·6.

$C_6H_5 \cdot SeO_2Na, 2H_2O$ (247·2) requires $H_2O = 14·6$ per cent.
Found, in anhydrous salt, $Se = 37·9$, $37·5$.*

$C_6H_5 \cdot SeO_2Na$ requires $Se = 37·5$ per cent.

Salts of Phenylselenic Acid.

Stoecker and Krafft (*loc. cit.*) prepared phenylselenic acid by the oxidation of diphenyl diselenide with moist chlorine, Doughty by the method given above (*loc. cit.*). The potassium salt can be obtained conveniently by oxidising phenylselenious acid with

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* For the estimation of selenium in the compounds described in this paper Frerichs's method (*Arch. Pharm.*, 1902, **240**, 656) was employed.

potassium permanganate, removing manganese dioxide, and evaporating to low bulk, when it crystallises from the solution.

Potassium phenylselenate forms colourless, prismatic needles which, after being dried in the air, sinter from about 50° and melt from 65° to 90° in the water of crystallisation. It is readily soluble in cold, and very readily so in hot, water.

Found, loss in a vacuum over H_2SO_4 and then at 100°, 12·7.

$C_6H_5 \cdot SeO_3K, 2H_2O$ (279·4) requires $H_2O = 12·9$ per cent.

Found, in anhydrous salt, $Se = 32·2$.

$C_6H_5 \cdot SeO_3K$ requires $Se = 32·6$ per cent.

Sodium phenylselenate was prepared from the barium salt, which has been described by Doughty (*loc. cit.*), by double decomposition with sodium sulphate. It crystallises from water in long, clear, oblong plates which contain $3H_2O$, and is readily soluble in cold, very readily so in hot water.

Found, in air-dried salt: loss at 120° = 24·2; $Se = 26·5$.

$C_6H_5 \cdot SeO_3Na, 4H_2O$ (299·2) requires $H_2O = 24·1$; $Se = 26·5$ per cent.

m-*Nitrophenylselenious Acid*, $NO_2 \cdot C_6H_4 \cdot SeO_2H$.

Phenylselenious acid did not yield a nitro-derivative when treated with a mixture of sulphuric and nitric acids at 100°. When subjected to the action of a large excess of fuming nitric acid at 150° for one hour, it gave a 20 per cent. yield of *m*-nitrophenyl-selenious acid. The best method for the preparation of this acid, however, was found in the action of nascent nitric acid generated from potassium nitrate.

Thirty grams of phenylselenious acid nitrate were dissolved in 30 c.c. of sulphuric acid, and the solution was cooled with running water. Twelve grams of finely powdered potassium nitrate were then stirred into the solution, which was similarly cooled. The mixture was heated for two hours in the steam-bath, and poured into 600 c.c. of water. After keeping for several hours, the separated crystals were collected. They amounted to 17·4 to 18·7 grams of an almost pure product melting at 155° or slightly lower.

m-*Nitrophenylselenious acid* crystallises from water in yellow, prismatic needles, which melt at 156—157° (corr.) after drying at 100°. It is fairly readily soluble in boiling water, sparingly so in cold.

Found, loss at 100° = 0·4; in dried substance, $C = 30·8$; $H = 2·2$.

$C_6H_5O_4NSe$ (234·2) requires $C = 30·8$; $H = 2·2$ per cent.

m-Nitrophenylselenic Acid, $NO_2 \cdot C_6H_4 \cdot SeO_3H$.

Thirty-five grams of *m*-nitrophenylselenious acid were dissolved in 600 c.c. of boiling water to which 20 c.c. of 10 per cent. aqueous potassium hydroxide had been added, and mixed with a solution of 16 grams of potassium permanganate in 200 c.c. of hot water. Further small quantities of permanganate were then added until the red colour no longer quickly vanished. The manganese dioxide was removed by filtration, and the solution evaporated to low bulk and cooled, when potassium *m*-nitrophenylselenate crystallised out. After purification by recrystallisation from water, 34 grams were obtained.

Potassium m-*nitrophenylselenate* forms hard, yellow rosettes of flat needles. It is anhydrous, and is readily soluble in hot, but somewhat sparingly so in cold, water. It explodes violently at about 330° (corr.).

Found: $Se = 27 \cdot 1$.

$C_6H_4O_5NKSe$ (288·3) requires $Se = 27 \cdot 5$ per cent.

Barium m-*nitrophenylselenate* was prepared from the potassium salt by double decomposition with the calculated quantity of barium chloride. It forms colourless leaflets which are fairly readily soluble in hot, but sparingly so in cold, water. It contains $2H_2O$, which are lost at 120°, but not at 110°.

Found, in air-dried salt, loss at $120° = 5 \cdot 6$. $Ba = 20 \cdot 2$.

$C_{12}H_8O_{10}N_2BaSe_2,2H_2O$ (671·9) requires $H_2O = 5 \cdot 4$; $Ba = 20 \cdot 5$ per cent.

m-Nitrophenylselenic acid was prepared from the barium salt by the addition of the calculated quantity of sulphuric acid, removal of barium sulphate, and evaporation to a syrup, when it crystallised, on keeping, in colourless plates containing $2H_2O$. The air-dried acid melts below 100°, but after drying first in a vacuum over sulphuric acid, then at 100°, it is rendered anhydrous and then melts at 146° (corr.).

Found, loss at $100° = 12 \cdot 8$.

$C_6H_5O_5NSe,2H_2O$ (286·3) requires $H_2O = 12 \cdot 7$ per cent.

0·2379, dried at 100°, required 18·95 c.c. of $N/20$-NaOH for neutralisation, whence equivalent = 251.

$C_6H_5O_5NSe$ requires M.W. = 250·3.

*Di-*m-*nitrophenyl Diselenide*, $(NO_2 \cdot C_6H_4 \cdot Se)_2$.

Twenty-four grams of *m*-nitrophenylselenious acid were dissolved in 250 c.c. of boiling water, and a saturated solution of sodium

hydrogen sulphite was added so long as a turbidity was produced. After cooling and stirring, the oil which had separated became crystalline, and was collected and washed with water. The theoretical yield—20·5 grams—was obtained, and the product melted at 79°. After crystallisation from ether, this compound formed yellow spears which melted at 83° (corr.).

Found: C=35·6; H=2·2.

$C_{12}H_8O_4N_2Se_2$ (402·5) requires C=35·8; H=2·0 per cent.

It is insoluble in water, moderately readily soluble in cold alcohol or ether, fairly readily so in hot alcohol, and easily so in hot ether.

Di-m-aminophenyl Diselenide, $(NH_2 \cdot C_6H_4 \cdot Se)_2$.

Fifty grams of di-m-nitrophenyl diselenide were added to a solution of 300 grams of commercial hydrated sodium sulphide in 500 c.c. of 10 per cent. aqueous sodium hydroxide previously heated to about 60°, and the mixture was boiled for one hour under a reflux condenser. One litre of boiling water was then added, and an excess of concentrated hydrochloric acid. After digestion for two hours on the steam-bath, the separated sulphur was removed by filtration. The filtrate was cooled, basified with sodium carbonate, and extracted with ether. The ethereal solution was dried with anhydrous potassium carbonate and distilled. The residue was mixed with an excess of 10 per cent. hydrochloric acid, when 39·7 grams of di-m-aminophenyl diselenide dihydrochloride separated in sandy crystals.

Di-m-*aminophenyl diselenide dihydrochloride* crystallises from dilute hydrochloric acid in yellow grains formed of small needles. It melts and decomposes at 291—292° (corr.). It is readily soluble in hot, but sparingly so in cold, dilute hydrochloric acid.

Found, loss at 100°=1·1; in dried salt, C=35·3; H=3·5; Se=37·5; Cl=16·8.

$C_{12}H_{12}N_2Se_2,2HCl$ (415·4) requires C=34·7; H=3·4; Se=38·1; Cl=17·1 per cent.

Di-m-acetylaminophenyl Diselenide, $(CH_3 \cdot CO \cdot NH \cdot C_6H_4 \cdot Se)_2$.

25·2 Grams of di-m-aminophenyl diselenide dihydrochloride were converted into the base, and this was treated with 25 c.c. of acetic anhydride. The clear liquid quickly began to crystallise, and soon set to a yellow, chalky mass, which was washed well with ether and dried in the air. 19·6 Grams of di-m-acetylaminophenyl diselenide

melting at 180° were thus obtained, the yield amounting to 76 per cent. of the theoretical.

For the preparation of this substance, the previous isolation of di-m-aminophenyl diselenide as the dihydrochloride is unnecessary; thus 91 grams of di-m-nitrophenyl diselenide were reduced by the method given previously, and the ethereal residue of crude di-m-aminophenyl diselenide was mixed with 50 c.c. of acetic anhydride and treated as above. The resulting di-m-acetylaminophenyl diselenide melted at 179° and amounted to 76 grams, that is, 79 per cent. of the theoretical.

Di-m-acetylaminophenyl diselenide crystallises from glacial acetic acid in rosettes of short, yellow needles which melt at 185—186° (corr.). It is anhydrous, and is insoluble in hot or cold water, almost insoluble in hot or cold ether, readily soluble in hot alcohol or glacial acetic acid, but sparingly so in these solvents when cold.

Found : C = 45·0 ; H = 4·0.

$C_{16}H_{16}O_2N_2Se_2$ (426·6) requires C = 45·0 ; H = 3·8 per cent.

Formation of Di-m-aminophenyl Diselenide by the Reduction of m-Nitrophenyl Selenocyanate.

m-Nitroaniline (6·9 grams) was diazotised in dilute hydrochloric acid solution at 0°, and, after filtering from 1 gram of diazoaminocompound, the acidity of the solution to Congo paper was removed by the addition of 10 grams of sodium acetate crystals. Potassium selenocyanate (7·2 grams) dissolved in a little water was added slowly with stirring. There was a brisk evolution of nitrogen accompanied by the separation of a red oil. On washing with water, the latter gradually solidified, and was dissolved in ether to free it from selenium powder (0·6 gram). The ethereal solution was concentrated, again filtered from a small quantity of a viscous red oil, and finally evaporated to a syrup, which crystallised on stirring. The product consisted of transparent crystals embedded in a small quantity of a deep red gum. The yield of crude m-nitrophenyl selenocyanate was 7·2 grams, or 73 per cent. of theory.

The crude product (3·4 grams) was dissolved in hot alcohol (50 c.c.) and reduced by boiling for one hour with tin (3·5 grams) and hydrochloric acid (45 c.c.; 32 per cent.). On concentration under diminished pressure, the hot solution deposited an orange-yellow, granular, crystalline stannichloride (5·8 grams).

One gram of the stannichloride was dissolved in water, and the tin removed as sulphide. The solution, on concentration, gave two

successive separations of crystalline di-*m*-aminophenyl diselenide dihydrochloride, 0·2 gram and 0·25 gram, each melting at 278—280° (uncorr.). (Found: Cl=17·0. Calc.: Cl=17·1 per cent.) Di-*m*-aminophenyl diselenide dihydrochloride, obtained by the reduction of di-*m*-nitrophenyl diselenide, melted at the same temperature as did a mixture of the two. Moreover, both form a sparingly soluble, primrose-yellow stannochloride crystallising in microscopic needles, and a stannichloride which tends to separate as an oil from cold solutions, but in granular crystals from hot solutions.

Acetylation of the di-*m*-aminophenyl diselenide, prepared from *m*-nitrophenyl selenocyanate, gave di-*m*-acetylaminophenyl diselenide in short needles which melted at 183—185° (uncorr.), the acetyl derivative of the reduction product of di-*m*-nitrophenyl diselenide melting at the same temperature, whilst a mixture of the two showed no depression of the melting point.

m-Acetylaminophenylselenious Acid, $CH_3 \cdot CO \cdot NH \cdot C_6H_4 \cdot SeO_2H$.

Ten grams of di-*m*-acetylaminophenyl diselenide were added with stirring in quantities of about 1 gram to 40 c.c. of nitric acid (D 1·4) kept at −6° to −3°. At first, the diselenide dissolved, giving a clear solution, but the separation of white crystals soon commenced, and increased on the further addition of this substance. The crystals were collected on asbestos, washed with concentrated nitric acid, and drained on porous porcelain. This substance melted at 146°, and was the nitrate of *m*-acetylaminophenylselenious acid. After grinding it with water, filtering, and washing with water, crude *m*-acetylaminophenylselenious acid, melting at 201°, remained undissolved. The product at this stage still contained nitric acid, and a portion, on boiling with water with the view of recrystallising it, readily oxidised. The whole was therefore dissolved in an excess of hot dilute ammonia (200 c.c.), treated with animal charcoal, filtered, and acidified with glacial acetic acid. On keeping, *m*-acetylaminophenylselenious acid crystallised in fine, colourless needles, which were collected, washed well with water, and dried in the air. The yield amounted to 8·5 grams of the pure acid.

m-Acetylaminophenylselenious acid crystallises from boiling water in short, slender, colourless needles, which begin to turn brown at about 200° and melt and decompose at 209° (corr.). It is sparingly soluble in hot, very sparingly so in cold, water.

Found: C=39·5, 39·5; H=3·7, 3·8.

$C_8H_9O_3NSe$ (246·3) requires C=39·0; H=3·7 per cent.

Sodium m-*acetylaminophenylselenite* crystallises from water in microscopic needles. After drying in the air, this salt contains $7H_2O$, of which 4 are lost at $100°$ and the remainder at $120°$. It is fairly readily soluble in cold and easily so in hot water.

Found: loss at $100° = 18·2$; loss at $120° = 32·2$.

$C_8H_8O_3NNaSe,7H_2O$ (394·4) requires $4H_2O = 18·3$; $7H_2O = 32·0$ per cent.

<div align="center">

Salts of m-*Acetylaminophenylselenic Acid,*
$CH_3 \cdot CO \cdot NH \cdot C_6H_4 \cdot SeO_3H.$

</div>

Fifty-five grams of *m*-acetylaminophenylselenious acid were dissolved in 70 c.c. of 10 per cent. ammonia and a litre of hot water, and mixed with a hot aqueous solution of 26 grams of potassium permanganate. After digestion for a few minutes on the water-bath, the slight excess of permanganate was reduced by means of alcohol. The solution was boiled, filtered from manganese hydroxide, and 28·5 grams of barium nitrate were dissolved in it. On evaporating to a small volume and keeping, barium *m*-acetylamino-phenylselenate crystallised out. After recrystallisation from water, 48 grams of the pure salt were obtained. A considerable further quantity was subsequently isolated from the mother liquors.

Barium m-*acetylaminophenylselenate* crystallises from water in hard, colourless, flat needles containing $4H_2O$. It is fairly readily soluble in cold, very readily so in hot, water.

Found: loss at $120° = 10·1$.

$C_{16}H_{16}O_6N_2BaSe_2,4H_2O$ (732·0) requires $H_2O = 9·8$ per cent.

Found, in dried salt, $Ba = 20·8$.

$C_{16}H_{16}O_6N_2BaSe_2$ requires $Ba = 20·8$ per cent.

Sodium m-*acetylaminophenylselenate* was prepared from the barium salt by double decomposition with sodium sulphate. It crystallises from water in colourless, woolly needles, and from alcohol in prismatic needles, in both cases without solvent of crystallisation. It is very readily soluble in water, sparingly so in cold alcohol, but fairly readily so in hot alcohol.

Found: $Se = 27·9$.

$C_8H_8O_4NNaSe$ (284·2) requires $Se = 27·9$ per cent.

<div align="center">

m-*Aminophenylselenic Acid,* $NH_2 \cdot C_6H_4 \cdot SeO_3H.$

</div>

Forty-five grams of barium *m*-acetylaminophenylselenate were dissolved in 500 c.c. of boiling water, and sufficient sulphuric acid

was added exactly to remove the barium. The solution was then boiled, filtered from barium sulphate, and evaporated to a small volume under diminished pressure, when 13 grams of *m*-amino-phenylselenic acid crystallised from the solution.

m-*Aminophenylselenic acid* crystallises from water in colourless needles which contain $2H_2O$, and, after drying at 100°, melts and decomposes at 229° (corr.). It is readily soluble in hot, sparingly so in cold, water.

Found, in air-dried substance, loss at 100° = 11·4.

$C_6H_7O_3NSe,1\frac{1}{2}H_2O$ requires $H_2O = 10·9$ per cent.

Found, in dried substance, C = 32·7; H = 3·3.

$C_6H_7O_3NSe$ (220·3) requires C = 32·7; H = 3·2 per cent.

Sodium m-*aminophenylselenate* crystallises from water in plates, which are readily soluble in cold water.

Found, in air-dried salt, loss at 120° = 19·9.

$C_6H_6O_3NNaSe,3\frac{1}{2}H_2O$ requires $H_2O = 20·6$ per cent.

Found, in dried salt, Se = 33·0.

$C_6H_6O_3NNaSe$ (242·2) requires Se = 32·7 per cent.

THE WELLCOME CHEMICAL WORKS,
DARTFORD, KENT.

XX.—*The* n-*Butylarylamines. Part III. Constitution of the Nitro-derivatives of* n-*Butyl-*p-*toluidine.*

By JOSEPH REILLY and WILFRED JOHN HICKINBOTTOM.

IN Part II. of this series (T., 1918, **113**, 985), the preparation of 2- and 3-nitro-*n*-butyl-*p*-toluidines was described, and in the present paper an account is given of the products of reduction of these nitro-compounds, the study of which has shown that the constitutions previously assigned to them are correct.

The 3-nitro-derivative, on reduction, furnishes 3:4-*tolylene*-4-N-*n*-*butyldiamine* (I), which is a readily oxidisable oil, and the corresponding 3-nitroacetyl derivative gives 2:5-*dimethyl*-1-n-*butyl*-*benziminazole* (II), which is also obtained by the action of heat on 4-*acetyl*-3:4-*tolylene*-4-N-n-*butyldiamine* (III).

(I.)   (II.)   (III.)
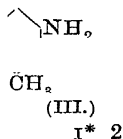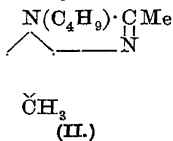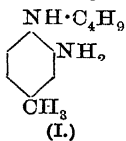
The constitution of 3 : 5-dinitro-*n*-butyl-*p*-toluidine is proved by the fact that on hydrolysis with sodium hydroxide it yields *n*-butyl-amine and 3 : 5-dinitro-*p*-cresol.

By the action of acids or direct sunlight on 3 : 5-dinitro-*p*-tolyl-*n*-butyl-nitro- or -nitroso-amine, the dinitro-amine is regenerated, and the nitroamine is similarly decomposed on boiling it with ethyl or *n*-butyl alcohols. When the nitroamine is hydrolysed by sulphuric acid or sodium hydroxide, nitrous acid is formed.

<p align="center">Experimental.</p>

2 : 4-*Tolylene*-4-N-*n*-butyldiamine, CH_3〈 $\overset{NH_2}{}$ 〉$NH \cdot C_4H_9$.
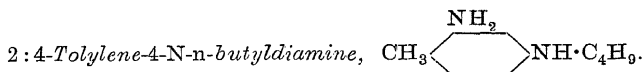
2-Nitro-*n*-butyl-*p*-toluidine (3 grams) was mixed with 10 c.c. of concentrated hydrochloric acid and 40 c.c. of water, and zinc dust (4 grams) gradually added. Excess of zinc was removed from the colourless solution, and the amine was isolated by the addition of sodium hydroxide solution, followed by extraction with ether. It formed a pale brown powder, which was purified by solution in dry ether and precipitation with light petroleum. A white, flocculent mass was obtained which, on drying, could easily be powdered. By spontaneous evaporation of the ethereal solution, it was obtained in colourless needles melting at 53°:

0·0956 gave 12·9 c.c. N_2 at 19·2° and 750 mm. $N = 15·56$.*

$C_{11}H_{18}N_2$ requires $N = 15·72$ per cent.

2 : 4-*Tolylene*-4-N-*n*-butyldiamine is soluble in most of the common organic solvents, sparingly so in water, and very sparingly so in light petroleum. With ferric chloride solution, it gives a very faint brown coloration, which, however, is not very characteristic. It gives no characteristic colour with nitrous acid or potassium ferrocyanide. The *hydrochloride* is very readily soluble in water.

4-*Acetyl Derivative*.—Tin foil was added to 2-nitroaceto-*n*-butyl-*p*-toluidide (1 mol.) suspended in concentrated hydrochloric acid (6 mols.) until reduction was complete. The solution was filtered, diluted with water, and the tin removed by means of hydrogen sulphide. The filtrate was rendered alkaline and the amine isolated, as a brown oil, by extraction with ether. It solidified to a mass of brown crystals, which on crystallisation from a mixture

* In the nitrogen estimations recorded in this paper, the gas was collected over 40 per cent. potassium hydroxide solution. A correction has been introduced for the vapour tension of the potassium hydroxide solution.

of ether and light petroleum was obtained in white crystals melting at 98—99°:

0·0723 gave 8·1 c.c. N_2 at 20° and 749 mm. $N = 12·87$.
$C_{18}H_{20}ON_2$ requires $N = 12·72$ per cent.

The compound dissolves in ether and many of the other organic solvents, but is insoluble in light petroleum. The diazo-compound gives with β-naphthol a brownish-red *azo-dye*, which dissolves in sulphuric acid with the development of a deep purple-red coloration, changing to pale brown on dilution. The *picrate* of the base crystallises from alcohol in groups of yellow needles melting at 185°.

3 : 4-*Tolylene*-4-N-n-*butyldiamine*.

The reduction of 3-nitro-*n*-butyl-*p*-toluidine in the way described for the 2-nitro-compound, yields the corresponding diamine as an oil, which is white when first precipitated, but rapidly acquires a deep blue colour and ultimately becomes almost black:

0·1211 gave 16·2 c.c. N_2 at 22° and 764 mm. $N = 15·57$.
$C_{11}H_{18}N_2$ requires $N = 15·72$ per cent.

The compound is readily miscible with most of the ordinary organic solvents. The *hydrochloride* was obtained by passing a stream of dry hydrogen chloride into a solution of the base in dry xylene. The bulk of the xylene was decanted, ·and the rest removed by washing with light petroleum. After being dried at 100°, the salt formed a white powder. It is extremely deliquescent and very readily soluble in water:

0·0552 gave 0·0625 AgCl. $Cl = 28·0$.
$C_{11}H_{18}N_2,2HCl$ requires $Cl = 28·2$ per cent.

The aqueous solution is very readily oxidised. One drop of ferric chloride solution produces an intense blood-red or deep brown colour. A dilute solution of chromic acid or a very dilute neutral solution of potassium dichromate produces a brownish-black or black solution, depending on the concentration of the oxidising agent. An aqueous solution of bleaching powder yields a deep blue solution. Nitrous acid in dilute solution gives a dirty purple coloration, whilst concentrated nitric acid also gives a purple coloration.

The 3 : 4-*diacetyl* derivative was prepared by warming the base with acetic anhydride. A dark-coloured oil was obtained, which slowly solidified to a mass of dark brown crystals. By repeated crystallisation from a mixture of light petroleum and acetone, or

from hot dilute aqueous alcohol, it was obtained in white crystals melting at 130° :

0·0754 gave 7·1 c.c. N_2 at 25° and 748 mm.   N = 10·62.

$C_{15}H_{22}O_2N_2$ requires N = 10·69 per cent.

The compound is moderately soluble in hot, but sparingly so in cold   water.

4-*Acetyl*-3 : 4-*tolylene*-4-N-n-*butyldiamine* (III).

3-Nitroaceto-*n*-butyl-*p*-toluidide (4   grams)   was   dissolved in 50 c.c. of aqueous alcohol (70 per cent.) containing iron filings (10 grams), and to the mixture, warmed to 30°, glacial acetic acid was slowly added, the temperature being kept at 30°.   After an hour, the mixture was heated on the water-bath, the unchanged iron removed by filtration, washed with warm dilute acetic acid, and the filtrate rendered alkaline and heated at 80° for several hours.   The base was extracted with ether and purified by re-crystallisation from a mixture of equal parts of dry ether and light petroleum, when it was obtained in short, colourless needles melting at 102° :

0·0702 gave 8·0 c.c. N_2 at 21° and 738 mm.   N = 12·85.

$C_{13}H_{20}ON_2$ requires N = 12·72 per cent.

The compound is readily soluble in alcohol, ether, benzene, or carbon tetrachloride, but very sparingly so in light petroleum. The diazo-compound gives a red *azo-dye* with β-naphthol.   On heating the base in a flask fitted with a short air condenser at 200° in an oil-bath, globules of water were observed in the condenser.   After heating for four to five hours, the dark, viscous residue was distilled over a free flame, when a pale yellow oil was obtained which did not solidify at 0°, and was not a primary amine. From its method of·formation, it is probably 2 : 5-*dimethyl*-1-n-*butylbenziminazole* (II).   The same compound was produced by the vigorous reduction of 3-nitroaceto-*n*-butyl-*p*-toluidide in acid solution.

The nitro-compound (5 grams) was dissolved in a mixture of glacial acetic acid (25 grams), concentrated hydrochloric acid (10 grams), and water (15 c.c.).   Zinc dust (20 grams) was added, and the solution became very warm.   After the reaction had moderated and more zinc dust had been added, the solution was heated on the sand-bath for one or two hours.   After removal of the excess of zinc, the solution was rendered alkaline with potassium hydroxide solution, and the precipitated oil extracted with ether.

On distillation, it was obtained as a very viscous, pale yellow oil boiling at 335—338°:

0·0746 gave 0·2115 CO_2 and 0·0606 H_2O. C = 77·34; H = 9·09.

0·0794 ,, 9·9 c.c. N_2 at 23·1° and 736 mm. N = 13·92.

$C_{13}H_{18}N_2$ requires C = 77·18; H = 8·97; N = 13·85 per cent.

2 : 5-Dimethyl-1-n-butylbenziminazole is miscible with ether or alcohol. When exposed in an open dish to a moist atmosphere, it readily absorbs water and oxygen, gradually becoming darker. By the action of an aqueous-alcoholic solution of picric acid on the alcoholic solution of the anhydro-base, the *picrate* was precipitated; this crystallised from acetone in short, yellow needles or prisms melting at 209°:

0·0756 gave 10·7 c.c. N_2 at 21° and 749 mm. N = 16·20.

$C_{13}H_{18}N_2, C_6H_3O_7N_3$ requires N = 16·24 per cent.

It is practically insoluble in water, ether, or alcohol.

Action of Alkalis on 3 : 5-*Dinitro*-n-*butyl*-p-*toluidine.*

The dinitro-compound (1 gram) was heated under reflux with a solution of 5 grams of potassium hydroxide in 40 c.c. of water for six to eight hours. The colour of the solution changed rapidly through brownish-red to very dark red or almost black. On distillation into dilute hydrochloric acid, n-butylamine hydrochloride was obtained. The alkaline residue in the flask, after being cooled and filtered, was acidified with dilute sulphuric acid, and from the ethereal extract a solid crystallising in yellow needles (m. p. 82°) was obtained, which proved to be 3 : 5-dinitro-p-cresol.

Action of Acids on 3 : 5-*Dinitro*-p-*tolyl*-n-*butyl-nitroamine and* -*nitrosoamine.*

3 : 5-Dinitro-p-tolyl-n-butylnitroamine (0·5 gram) was dissolved in 2 c.c. of concentrated sulphuric acid (97 per cent.), the solution being kept cool by immersion in ice-cold water. The nitroamine dissolved slowly with the production of a deep reddish-purple colour, which changed finally to yellow. After half an hour, the mixture was poured on ice, when a yellow solid was obtained, which proved to be the corresponding nitrosoamine. Nitrous acid was also found to be present. In another experiment, 50 c.c. of slightly warmed sulphuric acid (90 per cent.) were added to the nitroamine (0·5 gram). There was a faint odour of nitrous acid, and the colour changes were the same as those described above.

After remaining for twenty days, exposed for part of the time to sunlight, the colour had changed to deep red. On pouring into water and extracting with ether, 3:5-dinitro-*n*-butyl-*p*-toluidine was obtained as the chief product. Further, the nitroamine (0·5 gram) was heated under reflux with a mixture of concentrated hydrochloric acid (20 c.c.) and *n*-butyl alcohol (50 c.c.) for eight hours. The colour of the mixture gradually became darker until it was finally a deep red. After removal of the alcohol, a red substance melting indefinitely at 65—80° was obtained. The melting point was raised to 86—88° by treatment with amyl nitrite in the presence of hydrochloric acid, the colour also becoming considerably paler.

On warming the nitroamine with an aqueous solution of perchloric acid and allowing the mixture to remain for twelve hours, a slight darkening occurred. The action of glacial phosphoric acid in the cold produced practically no colour change after a week.

3:5-Dinitro-*p*-tolyl-*n*-butylnitrosoamine, by the action of hydrochloric acid containing some aniline hydrochloride, yields the corresponding amine in almost quantitative yield and in a pure condition (compare Pinnow, *Ber.*, 1897, **30**, 838). The nitrosoamine (2·4 grams) was heated under reflux for eight hours with alcoholic hydrogen chloride (50 c.c.) containing aniline hydrochloride (1 gram). On evaporating the alcohol, 2·1 grams of 3:5-dinitro-*n*-butyl-*p*-toluidine, identified by the mixed melting-point method, were obtained. When the aniline hydrochloride was omitted, the reaction followed a similar course, but required a longer time for completion.

Action of Alkalis on 3:5-Dinitro-p-tolyl-n-butyl-nitroamine and -nitrosoamine.

Alcoholic potassium hydroxide reacts with alcoholic solutions of the nitroamine and nitrosoamine with the production of a dark purple colour, which gradually deepens in intensity. In aqueous solution, the reaction takes place much more slowly. 3:5-Dinitro-*p*-tolyl-*n*-butylnitroamine (1 mol.) was heated under reflux with a large excess of a 10 per cent. aqueous solution of sodium hydroxide (15 mols.). The nitroamine was slowly attacked, yielding a purple solution which gradually became almost black, when the reaction was considered to be complete. On distillation, *n*-butylamine was obtained. The alkaline residue in the flask, which contained sodium nitrite, was diluted, and, after filtering, rendered acid in the presence of carbamide to remove nitrous acid. On extraction

with ether, a pale brown oil was obtained, which solidified to a yellow, crystalline solid. After several crystallisations from aqueous alcohol, this melted at 82°, and was shown to be 3:5-di-nitro-*p*-cresol.

When either the nitroamine or the nitrosoamine ·was heated with two or three times its weight of phenol at 180°, and the product treated with very dilute ice-cold sodium hydroxide solution, followed by extraction with ether, 3:5-dinitro-*n*-butyl-*p*-toluidine was obtained in good yield, and the same result was obtained by heating the nitroamine or nitrosoamine with a large excess of *n*-butyl alcohol or ethyl alcohol for several hours in diffused light.

Both the nitroamine and nitrosoamine were finely powdered and exposed in glass and quartz vessels to direct sunlight. After one hour, the nitrosoamine had deepened considerably in colour, and the melting point was depressed. The nitroamine, on the other hand, changed colour only slowly, but there was sufficient action in both cases after one month's exposure to detect the presence of 3:5-dinitro-*n*-butyl-*p*-toluidine. In some of the reactions where the decomposition was not complete, the melting point alone was not a sufficient guide to determine the composition of the product. The colour affords an indication of the production of the parent amine, and this was confirmed by the evidence obtained by the action of amyl nitrite and of nitric acid. In the decomposition of the nitrosoamine or of the nitroamine, the production of the parent amine was assumed to have occurred when the action of amyl nitrite or nitrous acid in the presence of hydrochloric acid or acetic acid effected a considerable loss of colour, and when the melting point was altered. The action of fuming nitric acid in giving a product identical with the original nitroamine showed that the butyl group had not been removed and that only the nitroso-group linked to the aminic nitrogen atom had been affected.

XXI.—*Studies in Catalysis. Part X. The Applicability of the Radiation Hypothesis to Heterogeneous Reactions.*

By William Cudmore McCullagh Lewis.

In the previous papers of this series, the radiation hypothesis has been applied exclusively to reactions in homogeneous systems. A mode of applying the hypothesis to reactions in heterogeneous systems, including heterogeneous catalysis, having suggested itself to the author more than two years ago, it may not be out of place to indicate it briefly here.

In attempting to elucidate the mechanism of any chemical or physical process, two complementary methods of treatment may be employed. In the first, the process is considered from the point of view of the material or molecular changes involved; in the second, from the point of view of the concomitant or precedent energy exchanges. The radiation hypothesis belongs to the second method of treatment. The two methods are not distinct in the sense that the results obtained in one often furnish a clue to the solution of a difficulty met with in the other. It is necessary, however, to possess, in the first place, some information regarding the most probable material mechanism of the process considered before introducing considerations based on the energy exchanges involved. In the case of heterogeneous reactions and catalysis, Langmuir's theory of the spatial distribution of molecules and atoms at the interface between two phases will be adopted as a basis for the material changes occurring, the energy changes being then dealt with from the point of view of the radiation hypothesis.

Langmuir's theory (compare *J. Amer. Chem. Soc.*, 1916, **38**, 2221) is essentially an extension of the work of the Braggs on crystal structure.

The surface of a solid is regarded as a checker-board on which atoms or molecules of gases may be condensed by being united to certain atoms in the surface itself. This adsorption effect is ascribed directly to valency, in some cases the surface being almost entirely covered or saturated, in others only a small fraction of the surface being thus occupied. According to Langmuir, this surface layer does not consist of several layers of molecules or atoms in which the density varies continuously. Instead, the change from solid to homogeneous gas is abrupt. This is based on the idea that it is only a layer one molecule or atom in thickness

which would be held sufficiently firmly to the surface, especially at the moderately high temperatures at which heterogeneous reactions proceed in general with measurable velocity. Langmuir's experimental results support this view in many cases. When a gas molecule strikes a surface, it is in general condensed. The rate at which it evaporates depends on the chemical or specific nature of the molecule and of the layer of atoms in the surface of the solid. Thus nitrogen, in which the atoms are already very completely saturated, possesses only a feeble external field of force, and in the *molecular* form, therefore, will be only slightly adsorbed.

Langmuir has found that hydrogen in the *atomic* form, produced by heating a wire in dry hydrogen at very low pressures, has a remarkable tendency to be adsorbed, this being regarded as due to the unsaturated affinity of the hydrogen atom. Langmuir has calculated that in this case the adsorbed layer of gas is just one atom in thickness. Oxygen is likewise easily adsorbed by metallic (tungsten) filaments. This adsorbed layer is exceedingly stable, and is evidently distinct from the formation of the compound WO_3, which volatilises easily in comparison. On Langmuir's view, the oxygen is retained on the surface in the atomic form. A molecule or atom which is strongly adsorbed is capable of displacing one which is feebly adsorbed. Hence addition of a strongly adsorbed gas—which in certain cases may be the resultant of the reaction—may cover the surface of a solid more or less completely, the surface being thereby " poisoned " with respect to a reaction in which the reactants are only feebly adsorbed. Langmuir has given several instances of such effects. The essential point for our present purpose is the dissociation, partial or complete, which many substances undergo into the atomic state on being condensed on surfaces, the cause of such dissociation being the localised valencies or lines of force which hold the atoms of the condensed substance to certain atoms of the surface of the solid.*

So much for the nature of the material changes involved. We have now to see how far the radiation hypothesis may assist in extending this view of the mechanism of the process.

In general, the velocity constants of heterogeneous reactions are characterised by possessing smaller temperature coefficients than those which are possessed by reactions in homogeneous systems. This means, on the basis of the considerations developed in earlier papers, that the critical increment in the heterogeneous process is

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* The catalytic effect of traces of moisture in the activation of molecules and atoms, and therefore possibly of surfaces, is not considered in the present paper. The facts hitherto recorded point to the conclusion that water is effective where ions are required to enable the reaction to proceed.

less than it would be for the same process occurring in the homogeneous system. This, in fact, appears to be the basis of the accelerating or catalytic effect of a given surface as viewed from the energy required to effect the chemical change.

It has already been shown that the reactivity of a substance depends on the magnitude of its critical increment, that is, the amount of energy which must be added per molecule or per grammolecule, in excess of the average energy content, in order to bring the molecule into the active state.

The higher the critical increment, the smaller is the reactivity or rate of reaction of the substance. This increment is taken account of by the exponential term which appears in the velocity expression developed in previous papers. The term referred to is $e^{-E/RT}$, where E is the critical increment per gram-molecule, R the gas constant per gram-molecule, and T the absolute temperature. It is this quantity that governs the magnitude of the temperature coefficient of a reaction, and, as is evident, the greater the value of E the greater is the temperature coefficient.

Let us suppose that a given reaction occurs in a homogeneous system, the sum of the critical increments of the reactants being E_1, whilst the sum of the critical increments for the same reaction when a heterogeneous catalyst is present is E_2. Then $E_1 > E_2$. The ratio of the velocity constant in the presence of the catalyst to that when the catalyst is absent is given essentially by the ratio $e^{-E_2/RT}/e^{-E_1/RT}$ or $e^{(E_1-E_2)/RT}$. This is, in general, a large positive quantity; it may be referred to as the catalytic factor. Let us suppose that the process considered involves the dissociation of a gaseous molecule. If this occurs in the homogeneous phase, the critical increment is large, of the order of 50,000 to 100,000 calories per gram-molecule. This energy has to be supplied by absorption of the radiation present in the system, and the greater the amount of energy required the higher must be the temperature in order that a sufficient number of quanta of high frequency may be available. If, on the other hand, a catalyst is present which is capable of condensing or adsorbing the gas in the atomic form, then the energy required is essentially that of sublimation or de-sorption of the atomic resultants from the surface diminished by the energy of adsorption or condensation of the molecular reactant. Such effects are in general small, of the order 5000 to 10,000 calories per gram-molecule. Hence in this case the catalytic factor would be $e^{(50,000-5000)/RT}$, which for the temperature $T = 1000°$ would correspond with $e^{22\cdot5}$, or 10^{10} approximately. It is evident that the effect which we have been considering is of very great magnitude, and to this extent is in agreement with the known high efficiency

of heterogeneous catalysts. From the point of view of the energy changes involved, therefore, the action of a catalyst is to be ascribed to the substitution of relatively small energy terms of the nature of de-sorption or sublimation effects in place of true critical energies of activation or dissociation. In general, the problem is not so simple as the case just considered. Frequently more than one reactant is involved, and in some cases partial activation or polarisation of one or more of the reactants may be effected without such reactant coming into direct contact with the surface of the solid itself. This will naturally occur when the surface is already covered by a reactant which possesses high capacity of adsorption. In general, however, the function of the catalyst is to bring at least one of the reactants into the active form, which would otherwise only be attained in the homogeneous phase by exceedingly high temperature conditions. The possibilities which present themselves will be rendered somewhat clearer by a preliminary examination of one or two actual cases.

The Reaction between Oxygen and Sulphur.

We shall first of all consider the reaction, $S + O_2 = SO_2$, as occurring in the homogeneous gaseous state.

Since the resultant contains two atoms of oxygen, the process does not require complete dissociation of the oxygen molecule as a preliminary step. Instead, a partial activation or polarisation of the oxygen molecule is sufficient. A value for this quantity may be obtained from a consideration of the thermal decomposition of ozone, which has been measured by Chapman and Jones (T., 1910, **97**, 2463), the reaction being shown to be bimolecular. The details of the calculation will be given in a subsequent paper, but it may be stated here that the critical increment of ozone per gram-molecule, obtained from Chapman and Jones's results, is 10,690 cals. Further, the heat evolved at constant volume when two gram-molecules of ozone decompose into three gram-molecules of oxygen has been determined with accuracy by Kailan and Jahn (*Zeitsch. anorg. Chem.*, 1910, **68**, 243), the value being 69,000 cals. Applying the quantum expression (compare T., 1917, **111**, 1086) to the process $2O_3 \longrightarrow 3O_2$, we obtain $69,000 = 3E'_{O_2} - 21,380$, whence $E'_{O_2} = 30,127$ cals., or 30,000 cals. in round numbers. The symbol E' denotes the critical increment per gram-molecule required for the partial activation or polarisation of oxygen which will permit three molecules thus activated to react to form two molecules of ozone. A molecule possesses, in general, different degrees or stages of activation, and this may not be the one required in the case of

the union of oxygen with sulphur. All partial activations are, however, small quantities compared with the activation required to cause complete dissociation of a molecule. So far as order of magnitude is concerned, the above value may be employed in this preliminary investigation.

We have now to consider the activation of sulphur vapour. In the temperature range 200° to 500°, the vapour of sulphur consists mainly of the molecular form S_8. Preuner and Schupp (*Zeitsch. physikal. Chem.*, 1909, **68**, 148) have measured the equilibrium of the reaction $4S_6 = 3S_8$. The mean value of the heat effect is 26,500 cals. This heat is absorbed in breaking down $3S_8$ molecules to $4S_6$ molecules. The same authors have obtained a fairly accurate value for the heat absorbed, namely, 58,000 cals., in the gaseous reaction $S_6 = 3S_2$. Hence the process $\frac{1}{6}S_6 \longrightarrow S_2$ requires an absorption of heat equal to 21,542 cals. We have now to consider the heat absorbed in the dissociation of S_2 into the atomic state. Budde (*Zeitsch. anorg. Chem.*, 1900, **78**, 169) has measured, by an explosion method, the equilibrium of the reaction $S_2 = 2S$, in the gaseous state, over the temperature range 2000° to 2500°. The results do not lead to an accurate value for the heat effect. Budde takes the value 120,000 cals. per gram-molecule. Von Wartenberg (*Zeitsch. anorg. Chem.*, 1908, **56**, 320) estimates the heat effect to be 90,000 cals. approximately. It has been shown (compare T., 1918, **113**, 471) that the critical increment in the case of the dissociation of a molecule into atoms is connected with the heat absorbed by the relation $-Q_v = E - \frac{1}{2}RT$. At $T = 2000°$, the value of E obtained from Budde's results is therefore 122,000 cals., but this is liable to considerable error. On the radiation hypothesis, this energy should be given by $Nh\nu$, where ν is the frequency of the light absorbed, N the number of molecules in one gram-molecule, and h Planck's constant. Martens (*Ann. Physik*, 1902, [iv], **8**, 603) has calculated that sulphur should possess a band in the ultra-violet region at $\lambda = 226\ \mu\mu$. The corresponding frequency is $13 \cdot 3 \times 10^{14}$, and therefore $Nh\nu$, or the critical increment per gram-molecule, should be 125,550 cals. This is remarkably close to the value calculated from Budde's data. In fact, the agreement is partly accidental. It is probable that the value obtained from Martens's data is the more correct. It follows that the heat of dissociation of diatomic sulphur into the atomic state in a gaseous system is 123,000 cals. per gram-molecule. Hence the energy absorbed in the process $\frac{1}{4}S_8 \longrightarrow 2S$ is $(123,000 + 21,540)$, or 144,500 cals. in round numbers. As might be expected, the chief factor in the total energy change from S_8 to atomic sulphur is the single process of dissociating the S_2 molecules. The critical increment

required to produce two gram-atoms of sulphur in the gaseous state from the corresponding quantity of S_8 molecules is 147,000 cals., and therefore the critical increment per gram-atom is 73,500 cals.

We have now to consider the formation of sulphur dioxide from oxygen and sulphur, the latter consisting of S_8 molecules, the system being entirely gaseous. The partial critical increment of the oxygen is taken to be 30,000 cals. per gram-molecule. Hence the total critical increment of the system $(S + O_2)$ under the conditions stated is $(73,500 + 30,000)$, or 103,500 cals. The heat of formation of sulphur dioxide from solid sulphur and gaseous oxygen is 69,400 cals. per gram-molecule (Berthelot) (compare Ferguson, *Proc. Nat. Acad. Sci.*, 1917, **3**, 371). The heat of vaporisation of sulphur is 12,000 cals. per gram-atom in round numbers. Hence the heat of formation of sulphur dioxide from its gaseous components is 81,400 cals. Employing the relation:

$$\text{Heat evolved} = E_{\text{resultants}} - E_{\text{reactants}},$$

we get $81,400 = E_{SO} - 103,500$, whence $E_{SO} = 184,900$ cals. per gram-molecule. It follows from this value that the frequency of the effective radiation is $19\cdot6 \times 10^{14}$, and the wave-length $\lambda = 153 \,\mu\mu$. Sulphur dioxide is known to have an absorption band in the extreme ultra-violet region beyond $200 \,\mu\mu$ (compare Garrett, *Phil. Mag.*, 1916, [vi], **31**, 505), but the position of the band has not as yet been located.

The above exceedingly high value for the critical increment of sulphur dioxide requires that the molecule should be correspondingly stable. Thus it should not be possible to decompose it into its components by a quartz mercury lamp, since quartz does not transmit wave-lengths longer than about $185 \,\mu\mu$. As an illustration of its stability, it may be mentioned that von Wartenberg (*loc. cit.*) was unable to detect any sensible dissociation of sulphur dioxide even at 2200° abs. For our present purpose, it is more important to observe that the critical increment of the reactants $(S + O_2)$ is also very high, namely, 103,500 cals.

The numerical values given above refer to the reaction non-catalysed. If, however, the reaction is carried out in the presence of solid or fused sulphur, heterogeneous catalytic effects enter. This has been shown experimentally by Bodenstein and Caro (*Zeitsch. physikal. Chem.*, 1910, **75**, 30), the sulphur acting as a positive catalyst. The result of the positive catalysis is that the critical increment of the system $(S + O_2)$ is much less than the value given above. From the temperature coefficient obtained by Bodenstein and Caro in the region of 250°, in the presence of solid sulphur, it is found that the critical increment of the reactants

$(S + O_2)$ lies between the limits 31,308 and 34,184 cals., the mean value being 33,000 cals. in round numbers.

It is possible to account approximately for the order of magnitude of the critical increment obtained, when heterogeneous catalysis occurs, by supposing that the oxygen is already activated at the temperature chosen before coming into contact with the sulphur surface, the increment of partial activation of oxygen being of the order 30,000 cals., as we have seen already. The sulphur itself is already in the atomic state in the surface layer of the solid, and consequently does not require further activation. The heat of volatilisation of the sulphur dioxide per gram-molecule is a quantity of the order 5000 cals., so that in all the apparent increment is of the order 35,000 cals., which agrees moderately well with that observed.

In the above case, the catalytic factor at 250° is $e^{(103,500-85,500)/RT}$ or $e^{68,000/RT}$, or 10^{28} approximately. These numbers are simply employed for purposes of illustration; sufficient data have not yet been accumulated to permit of more exact calculation.

If such changes in the critical increment are brought about as a result of catalytic effects, it is necessary to conclude that in general the heat effect of a process will be modified by the catalyst, and if this is the case the variation of the equilibrium constant of the reaction in the surface layer with temperature will be affected, so that finally the equilibrium constant of the catalysed reaction will differ from that of the non-catalysed reaction. This conclusion is in general agreement with that arrived at by Bancroft (*J. Physical Chem.*, 1917, **21**, 573) on false equilibria and the effect of heterogeneous catalysis on the position of the equilibrium.

The Union of Oxygen and Hydrogen.

Bodenstein (*Zeitsch. physikal. Chem.*, 1899, **29**, 665) has found that the temperature of the termolecular velocity constant, corresponding with the reaction $2H_2 + O_2 = 2H_2O$, is 1·75 for 10° over the temperature range 482° to 509°. The reaction proceeds under the conditions employed almost entirely at the surface of the porcelain containing-vessel. From the above value of the temperature coefficient, it would follow that the critical increment for two gram-molecules of hydrogen and one gram-molecule of oxygen is 66,000 cals., and therefore for one gram-molecule of hydrogen and one half-gram-molecule of oxygen the increment of the reactants is 33,000 cals. Bodenstein's results have, however, been criticised by Bone and Wheeler (*Phil. Trans.*, 1906, [*A*], **206**, 1), who find that the reaction is not termolecular, but approximately unimole-

cular, especially unimolecular with respect to the hydrogen. The reaction which appears to occur is therefore $H_2 + O = H_2O$. Bone and Wheeler have given data for the reaction from which the temperature coefficient and critical increment of the reactants may be calculated when nickel is the catalyst. For the temperature range 473° to 493° abs., the critical increment of the reactants ·is calculated to be 35,000 cals., which agrees fairly well with the value obtained from Bodenstein's results for the porcelain surface. Over the temperature range 493° to 513° abs., the results obtained by Bone and Wheeler give an increment of 52,000 cals. in round numbers. This is considerably greater than that obtained at the lower range of temperature, and indicates that the catalytic effect is relatively less efficient at the higher temperature, due, presumably, to diminished adsorption of the reactants. In both cases, however, the increment is a relatively small quantity, very much smaller than would be expected from the process occurring in the homogeneous phase, for the molecule of oxygen, which has to be dissociated, is very stable.

We have now to attempt to account for a quantity of the above order of magnitude on the basis of the energy—mechanism outlined. Let us assume, in the first place, that the oxygen is adsorbed and exists in the atomic state attached to certain positions on the surface of the catalyst. It is necessary that an activated or polarised molecule of hydrogen shall come into contact with an oxygen atom. It is only necessary for the hydrogen to be partly activated. Bohr (*Phil. Mag.*, 1913, [vi], **26**, 1, 476, 857) has investigated the energy changes which occur in the molecule and the atom of hydrogen in various processes involving the removal and addition' of an electron. Bohr has calculated that the process of transferring an electron so as to give rise to a system consisting of a positively charged hydrogen atom and a negatively charged one requires an absorption of energy of 21,000 cals. per gram-molecule of hydrogen. We shall employ this value in the present case, although' there is evidence that a somewhat higher value is probably more correct. The latent heat of vaporisation of water is in round numbers 9000 cals. per gram-molecule in the neighbourhood of 100°. As before, we shall assume that the heat of de-sorption of the water produced in the reaction is of the same order of magnitude. Hence we would expect the critical increment of the process to be of the order 30,000 cals. per gram-molecule of hydrogen and per gram-atom of oxygen. This agrees moderately with the observed value.

Sufficiently accurate data are not as yet available for calculating the critical increment of the reactants of the same reaction in the·

homogeneous gaseous state. It is necessary to dissociate the molecule of oxygen, and this appears to require a quantum of energy corresponding with approximately the region $\lambda = 200\,\mu\mu$, whence the critical increment per gram-molecule is of the order 140,000 to 150,000 cals. That is, the total increment of the reactants, reckoned per gram-molecule of hydrogen, is $21,000 + 140,000/2$, or 91,000 cals. The catalytic efficiency is therefore given by the ratio $e^{-33,000/RT}/e^{-91,000/RT}$ or $e^{58,000/RT}$. At 500° this factor is of the order 10^{17}. These figures are merely illustrative, but they serve to indicate the great influence on the velocity which is to be expected on the basis of the treatment suggested.

In dealing with the union of oxygen and hydrogen, it has been assumed above that the oxygen is condensed in the atomic form on the catalyst, the subsequent chemical change being $H_2 + O = H_2O$. From a number of observations made by Bone and Wheeler (loc. cit.), it appears that hydrogen is preferentially adsorbed. In such cases, the most probable reaction, because it involves the minimal critical increment, would be represented by $H_2 + O_2 = H_2O_2$, in which the hydrogen and oxygen are partly activated, but neither of them is completely dissociated. The formation of water would result from the subsequent decomposition of the hydrogen peroxide. The idea that hydrogen peroxide is an intermediate stage is, of course, not new. It appears from such considerations that the specific nature of the catalyst may determine the actual mechanism of a given reaction to a large extent.

The Union of Oxygen and Silicon.

In the reactions just considered, the critical increment of partial activation of oxygen has been taken to be 30,000 cals. approximately, this being the value required for the formation of ozone. As already pointed out, more than one stage of activation may be anticipated up to the limiting activation which corresponds with complete dissociation of the molecule into atoms. Each activation corresponds with a certain size of quantum of radiant energy, that is, with a certain frequency. The general conclusion reached in connexion with absorption spectra is that frequencies are related to one another in terms of even multiples of some fundamental frequency, that is, various degrees of activation are similarly related. A low degree of activation of the oxygen molecule requires 30,000 cals. of energy to be absorbed per gram-molecule, and therefore higher degrees of activation would require 60,000, 90,000 cals., etc., up to the limiting value of complete dissociation, which

appears to correspond with a quantity of the order 140,000 to 150,000 cals.

Sufficient information is not as yet available to enable us to say how many of these possible degrees of activation may actually manifest themselves. As an example of partial activation of oxygen which is apparently considerably greater than 30,000 cals., we may take the case of the formation and decomposition of an exceedingly stable compound, silica or quartz.

To decompose a molecule of quartz, it is evident that a quantum in the very extreme ultra-violet portion of the spectrum is required, in order to supply the necessary energy. It is well known that quartz commences to absorb radiation sensibly beyond the wave-length 185 $\mu\mu$. S. Richardson (*Phil. Mag.*, 1916, [vi], **31**, 463) finds that the dispersional wave-length of quartz is 105 $\mu\mu$. It does not necessarily follow that the dispersional wave-length or frequency is that required for complete dissociation of the molecule. That in the case of quartz, however, the necessary wave-length cannot differ much from 105 $\mu\mu$ is rendered probable by the following consideration. In a quartz mercury vapour lamp, it is generally believed that the quartz remains undecomposed; otherwise it would be difficult to account for the life and permanence of the lamp. That is, quartz can only be decomposed by a wave-length which is shorter than any emitted by the mercury vapour. O. W. Richardson and Bazzoni (*Phil. Mag.*, 1917, [vi], **34**, 285) have found that there is a limiting wave-length in the spectrum of a substance; that is, no wave-length shorter than a certain value, characteristic of the substance, can be emitted. In the case of mercury vapour, this limiting wave-length lies between 120 and 100 $\mu\mu$. The mean of these two limits is 110 $\mu\mu$, and we conclude on the above reasoning that quartz can only be decomposed by a wave-length shorter than this value. This points fairly definitely to S. Richardson's value, 105 $\mu\mu$, for the dispersional wave-length of quartz as being the wave-length capable of decomposing the molecule.

The critical increment corresponding with $\lambda = 105\ \mu\mu$ is 270,000 cals. per gram-molecule of quartz, an enormous quantity, which is in qualitative agreement with the known stability of quartz.

We have now to consider the heterogeneous reaction

$$Si + O_2 = SiO_2.$$
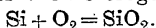
On Langmuir's view as applied in the present paper, we regard the silicon as already in the atomic state. If x is the necessary critical increment of oxygen per gram-molecule, then x is likewise the total critical increment of the reactants. The heat of the reaction is known to be 184,000 cals. in round numbers, and hence,

on applying the quantum–heat expression: heat evolved = critical increment of resultants − critical increment of reactants, we obtain $184,000 = 270,000 - x$, whence $x = 86,000$ cals. Owing to the error in the observed heat effect and in the value of the critical increment of quartz, this value for the critical increment of oxygen may be regarded as agreeing approximately with the value 90,000 cals. expected from the lower degree of activation of the molecule. What is particularly important is that even this value does not correspond with complete dissociation of the oxygen molecule. We may therefore conclude that the molecule of quartz possesses the structure $Si{<}^O_O$, rather than $O{:}Si{:}O$. This is an illustration of how a knowledge of the necessary critical increments —which in the present case, unfortunately, are not known with precision—may lead to information concerning molecular structure.

One of the chief difficulties met with in the kinetics of heterogeneous reactions has its origin in the selective nature of the absorbability of the reactants and the resultants, particularly the latter. The so-called catalytic "poisons" are now generally regarded as owing their effect to marked selective adsorption, as a result of which the surface of the catalyst becomes covered with a layer of molecules, and is thus no longer capable of catalysing the reaction. In many cases, the resultants of the reaction are adsorbed in this manner, and consequently function as a catalytic poison. Since the extent of adsorption diminishes as the temperature rises, it is obvious that when such poisoning effects are present the temperature coefficient of the reaction velocity over a certain range of temperature is not comparable with that over a different range, for the total observed velocity depends not only on the true effect of temperature on the chemical process itself, but likewise on the alteration in the extent of active surface presented to the reactants. The simplest conditions are obviously those in which the adsorption effects are a minimum, and such conditions will occur generally when the energy required for sublimation or desorption is small. In the other cases where adsorption effects are large, it is necessary to correct the observed velocity constants for the change in the area of the effective surface produced as a result of the change in temperature. Thus in the case in which the resultant is markedly adsorbed, and therefore acts as a negative catalyst, the temperature coefficient will possess too high a value, and instead of decreasing as temperature rises, may even increase. A similar abnormal behaviour is to be anticipated when a reaction proceeds partly in the homogeneous gaseous phase, partly in the

surface, for as the temperature rises the reaction tends to predominate in the gaseous phase, and therefore possesses a higher temperature coefficient.

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XXII.—*The Estimation of the Methoxyl Group.*

By JOHN THEODORE HEWITT and WILLIAM JACOB JONES.

SINCE the introduction of the Zeisel method for the estimation of methoxyl groups (*Monatsh.*, 1885, **6**, 989; 1886, **7**, 406; Benedikt and Grüssner, *Chem. Zeit.*, 1889, **13**, 872), numerous attempts have been made to simplify the apparatus and shorten the operation. The method of rectifying the methyl iodide proposed by Zeisel is effective but troublesome; the inclined condenser has to be of considerable length, and consequently occupies some bench space, whilst the constant supply of water to the condenser at about 50° necessitates supervision. A further inconvenience of the Zeisel method is the trouble experienced in working up the precipitate of double iodide and nitrate of silver, time being lost in evaporating the alcohol and obtaining the silver iodide in a pure condition.

The use of a rectifying column provided with a thermometer, in place of the inclined condenser fed with water at an approximately definite temperature, was recommended by Hewitt and Moore (T., 1902, **81**, 318), and impurities in the hydriodic acid were removed by passing carbon dioxide through the acid at 130° before introducing the substance under examination. Considerable saving in bench space was effected, and during the operation it was only necessary to control the stream of carbon dioxide and the flame under the glycerol bath so as to give the necessary temperatures in the reaction flask and at the top of the rectifying column. Several modifications of the Zeisel method have been suggested in which ordinary rectification has been relied on in place of inclined condensers in which the temperature is controlled by running water (Perkin, T., 1903, **83**, 1367; Zeisel and Fanto, *Zeitsch. anal Chem.*, 1903, **42**, 549; Stritar, *ibid.*, 579; Hesse, *Ber.*, 1906, **39**, 1142). Shortening the process by estimation of the methyl iodide in a more rapid manner was left untouched for years. The necessity of estimating methyl iodide obtained from methyl alcohol

mixtures rapidly and accurately caused the present authors to
search for a quick process.

Since combination of alkyl iodides with bases of the pyridine
series takes place very rapidly, there seemed to be a promising way
of obtaining the iodide in an ionisable form and then estimating
it volumetrically. After working out a satisfactory process, it was
found that the same fundamental idea of combining the methyl
iodide with a tertiary base had already been utilised (Kirpal and
Bühn, *Ber.*, 1914, **47**, 1084), but the subsequent volumetric
estimation of iodide by standard silver nitrate solution may be con-
siderably shortened. Instead of rejecting the excess of pyridine
by evaporation and estimating the iodide with standard silver
nitrate, using a chromate as indicator, the pyridine and its meth-
iodide may be directly diluted with water, acidified with nitric
acid, a known amount of silver nitrate added, and the excess of
the latter determined by thiocyanate according to Volhard's
method. Adoption of this procedure reduces the time of experi-
ment considerably.

The applicability of Volhard's method to the estimation of
methyl iodide after reaction with pyridine was controlled in a
separate experiment. 3·10 Grams of freshly distilled methyl iodide
were diluted to a volume of 100 c.c. with pyridine which had been
saturated with carbon dioxide. By dilution with water, addition
of silver nitrate, and determination of the excess of silver with
thiocyanate, 3·13 grams of methyl iodide per 100 c.c. were found.

Method.

Hydriodic Acid.—The hydriodic acid is prepared by saturating
an aqueous suspension of iodine with hydrogen sulphide, distilling
the resulting solution, and collecting the fraction boiling between
123° and 127° (D 1·7) for use.

Residues from analyses are redistilled and used again.

Pyridine.—Complete separation from picoline is unnecessary;
it is, however, advisable to remove substances of high boiling point.
* Pyridine bases as obtained from tar distillers are mixed with
two-thirds of their weight of water and fractionated. The fraction
distilling between 93° and 97°, containing the mixture of constant
boiling point, is shaken with one-third of its weight of solid sodium
hydroxide, the upper layer is separated, fractionally distilled, and
the bases distilling between 114° and 117° are collected for use.
Residues containing pyridine may be accumulated, rendered alkaline
with one-fiftieth of their weight of solid sodium hydroxide, distilled,
the distillate at 93—97° collected, and worked up.

The Estimation.—The apparatus consists of the usual carbon dioxide generator, decomposition flask heated in a glycerol bath to 130°, and rectifying column (four-pear or other suitable form). The carbon dioxide carrying the methyl iodide vapour is passed through two test-tubes in series, each containing 10 c.c. of pyridine.

For the estimation, a suitable weight of the substance is taken, and 20 c.c. of hydriodic acid (D 1·7) are added.

After the experiment has been in progress for one hour, the contents of the test-tubes are completely washed into a graduated flask, when they are diluted with water, and the iodide is estimated by the process indicated above.

In all cases, early in the course of the experiment, a yellow coloration develops in the pyridine. This vanishes on diluting the pyridine at the end of the experiment. Its appearance, therefore, need cause no apprehension to the analyst that free iodine is finding its way into the pyridine. Moreover, carefully purified samples of methyl iodide and pyridine on admixture develop colour. The behaviour of a mixture on dilution with water was compared with that of an iodine solution of equal depth of colour. On diluting a 3 per cent. solution of methyl iodide in pyridine with a quarter of its volume of water, the colour became very pale, and with its own volume of water it almost vanished. The iodine solution, on being similarly diluted, still retained its colour. It would thus appear that the coloration is not due to free iodine. Should, however, the colour persist on dilution with water, it is then advisable to discharge it with thiosulphate solution.

Analyses.

Substance.	Percentage of methoxyl group	
	Found.	Calculated.
Brucine hydrate	13·5	13·3
Methyl oxalate	50·1	52·5
Methyl alcohol	95·2	96·9
,, ,, ...	95·2	96·9
,, ,, ...	96·0	96·9
,, ,, ...	96·3	96·9
Methyl salicylate	19·7	20·4

A methylated cellulose which gave 39·1 per cent. of methoxyl by the gravimetric Zeisel method was found to contain 39·2 per cent. by the present method.

Unsatisfactory results were obtained with a sample of methyl benzoate and with one of hydrated quinine sulphate.

This comparatively rapid method for the estimation of methoxyl

groups may be applied conveniently to the products of wood distillation or other mixtures containing methyl alcohol.

Methyl alcohol has usually been estimated in these products by conversion into methyl iodide, and measurement of the volume of the latter compound (Krell, *Ber.*, 1873, **6**, 1310; Grodzky and Krämer, *ibid.*, 1492). Zeisel and Stritar's process of weighing volatilised iodine as silver iodide obviates the inexactness due to determination of the volume of the methyl iodide, but time may be saved by combining the methyl iodide with a tertiary base and estimating the iodine volumetrically.

A suitable amount (see below) of the liquid to be analysed is heated with 20 c.c. of hydriodic acid (D 1·7) for one hour. The contents of the test-tubes are then completely washed into a graduated flask and made up with water to 100 c.c. An aliquot portion (see below) of the diluted solution is introduced into a glass stoppered bottle of 250 c.c. capacity, 70 c.c. of water are added, and then, in order, 25 c.c. of $N/10$-silver nitrate solution and 30 c.c. of approximately $10N$-nitric acid. The bottle is well shaken by hand for five minutes, and 5 c.c. of concentrated ferric alum indicator are added. $N/10$-Thiocyanate solution is now run in until further addition of one drop imparts a permanent orange colour to the liquid.

Suitable amounts of liquids to be taken for analysis are given below.

a represents the volume of material to be operated on and its dilution when necessary.

b gives the volume of the diluted aqueous pyridine solution, obtained as described above, to be actually used in a titration.

c is the formula to be used giving the weight in grams of methyl alcohol in 100 c.c. of the liquor analysed, where *t* is the number of c.c. of $N/10$-thiocyanate solution used in the titration. (*Note.—*The figure 25 given in the formulæ must be multiplied by *f*, the factor for the silver nitrate solution, if this is not exactly decinormal.)

Pyroligneous Acid.—(a) Take 5 c.c. of the original liquor; (*b*) 40 c.c.; (*c*) 0·16 $(25-t)$.

Crude Wood Naphtha.—(a) Take 10 c.c., dilute to 100 c.c. with water, and use 5 c.c. of the diluted solution for distillation with hydriodic acid; (*b*) 40 c.c.; (*c*) 1·6 $(25-t)$.

Methyl Alcohol and Mixtures of the Alcohol with Acetone.— (*a*) Take 10 c.c., dilute to 100 c.c. with water, and use 5 c.c. of this diluted solution for the estimation; (*b*) 20 c.c.; (*c*) 3·2 $(25-t)$.

Analyses.

Artificial mixtures containing methyl alcohol and other products of wood distillation were made up and analysed by the method described.

Liquor Number.	Composition. No. of grams of methyl alcohol per 100 c.c. of liquor.	
	Actual.	Found.
1	2·39	2·35
2	68·5	68·1
3	2·39	2·35
4	31·8	31·5

Analyses of purified methyl alcohol by the present method have already been given.

It will be seen that, on an average, the results are 1 per cent. too low. Stritar and Zeidler (*Zeitsch. anal. Chem.*, 1904, **63**, 387) found that the maximum amount of methyl iodide obtainable from pure methyl alcohol in a Zeisel estimation corresponded with a 99 per cent. yield.

Liquors 1 and 2 were aqueous solutions of purified methyl alcohol. Liquor 3 contained, per 100 c.c., 7·03 grams of acetic acid, 0·80 gram of acetone, and 2·39 grams of methyl alcohol, the remainder being water. It represented a pyroligneous acid. Liquor 4 was an equilibrium mixture prepared from 10·04 grams of acetic acid, 39·60 grams of acetone, and 31·82 grams of methyl alcohol, made up to 100 c.c. with water (1·27 grams). This mixture, which, of course, contained methyl acetate, represented the first runnings obtained in the rectification of crude wood naphtha.

Compounds yielding Methyl Iodide, other than Methyl Alcohol, present in Wood Distillates.

The constituents of wood distillates have been examined by Stritar and Zeidler (*loc. cit.*) with a view to determine which yield methyl iodide on treatment with hydriodic acid. They found that acetone gave no methyl iodide, whilst the yield from both formaldehyde and acetaldehyde was negligible. Methyl acetate gave one equivalent of methyl iodide, and methylal and dimethylacetal each gave two. Allyl alcohol yielded its equivalent of *sec.*-propyl iodide. Guaiacol and other methyl derivatives of the phenols yielded their equivalent of methyl iodide.

Of these substances, the quantities of acetal encountered are too

small to be of consequence. According to Grodzki and Krämer (*loc. cit.*), the amounts of allyl alcohol and of methyl alcohol in raw wood spirit are in the ratio of 2 to 1000. Stritar and Zeidler find that guaiacol may be eliminated from aqueous solutions of crude wood spirit by shaking with animal charcoal. They state that on omitting this treatment, the amount of methyl alcohol found is too high by about 2 parts in 100 parts. It will be seen that the quantities of alkyl iodide yielded by the amounts of allyl alcohol and of guaiacol present in the aqueous wood distillates, relatively to that yielded by the methyl alcohol present, border closely on the experimental error. It is the experience of the authors that, where precautions are taken to eliminate these substances preliminary to analysis, the errors due to losses outweigh the error introduced through ignoring their presence.

The present method gives the total methyl alcohol, including both the free alcohol and that which is combined as methyl acetate. If it is desired, the amount of ester present may be determined by quantitative hydrolysis.

The alcoholic silver nitrate of the Zeisel method of estimating methoxyl may be replaced by pyridine. The pyridinium methyl iodide formed can be determined by Volhard's thiocyanate method.

Methyl alcohol in wood distillates may be determined by the method described above.

XXIII.—*The Preparation of Monomethylaniline.*

By Percy Faraday Frankland, Frederick Challenger, and Noel Albert Nicholls.

When aniline is submitted to the action of the usual methylating agents, it is difficult to limit the course of the reaction to the introduction of a single methyl group. We have investigated the production of monomethylaniline by three methods, with a view to obtain it in a pure condition.

(1) The process described in the German Patent 75854, and with slight modifications in the French Patent 212506, consists in condensing aniline with formaldehyde and then reducing with zinc dust and concentrated aqueous sodium hydroxide until a test portion dissolves to a clear solution in acetic acid. Any unreduced methyleneaniline, $CH_2{:}N{\cdot}C_6H_5$, is thereby converted into insoluble

anhydroformaldehydeaniline, $(CH_2{:}N{\cdot}C_6H_5)_3$. Using 100 grams of aniline, we have found the reduction to be completed in twelve to fifteen hours, and have obtained about 55 per cent. of the theoretical yield of methylaniline.   The Patent Specifications make no mention of the yields obtained.

The principal advantage of this method lies in the fact that the product, although rich in aniline, contains only traces of dimethylaniline.   The presence of the aniline may be the result of incomplete condensation with formaldehyde in the first instance, or of the hydrolysis of the methyleneaniline by the hot water, or of both causes.   The primary base can be recovered in the form of its zincichloride, which is almost insoluble in water, the methylated bases not being affected by this reagent (*Monatsh.*, 1888, **9**, 514). The method appears to work very satisfactorily.

Morgan (English Patent 102834), who has also studied the reduction of methyleneaniline, suggests that the poor yield of methylaniline may be due, in addition to hydrolysis, to the conversion of some of the methyleneaniline into *s*-diphenylmethylenediamine, $CH_2(NH{\cdot}C_6H_5)_2$, and anhydroformaldehydeaniline. We have failed to obtain more than traces of monomethylaniline from the last-named substance (compare, however, Goldschmidt, *Chem. Zeit.*, 1904, **28**, 1229), but when *s*-diphenylmethylenediamine (Eberhardt and Welter, *Ber.*, 1894, **27**, 1804; Eibner, *Annalen*, 1898, **302**, 349) is reduced with zinc dust and alkali hydroxide under the conditions of the earlier patents, aniline and monomethylaniline are produced in equal amounts, probably according to the equation

$$CH_2(NH{\cdot}C_6H_5)_2 + 2H = C_6H_5{\cdot}NH_2 + C_6H_5{\cdot}NH{\cdot}CH_3.$$
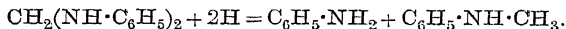
We attempted to diminish the hydrolysis by performing the reduction in concentrated alcoholic solution. The yield of methylaniline was, however, only about 46 per cent. No better results were obtained by increasing the quantity of formaldehyde; 1·5 molecular proportions gave rise to some dimethylaniline, whilst with 10 molecular proportions, considerable quantities of this base were formed.*

This appears to be due to the interaction of monomethylaniline and formaldehyde, giving rise to *s*-diphenyldimethylmethylenediamine, which then undergoes reduction.   This reaction would, moreover, be analogous to the reduction of *s*-diphenylmethylenediamine. The condensation product of formaldehyde and methyl-

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* Compare the action of formaldehyde on methylaniline in acid solution (Goldschmidt, *loc. cit.*) and on methyl-*o*-toluidine (Braun, *Ber.*, 1908, **41**, 2153), also on ammonium chloride (Werner, T., 1917, **112**, 844). See also Pinnow, *Ber.*, 1894, **27**, 3166; Cohn, *Chem. Zeit.*, 1900, **24**, 564.

aniline (Braun, *Ber.*, 1908, **41**, 2147) was therefore prepared and reduced under the usual conditions, with the result·that much dimethylaniline was produced.

(2) The process described in various works of reference consists in heating aniline hydrochloride with methyl alcohol in an autoclave to 180—200°.* The best result obtained by us in a series of thirteen experiments was a 55 per cent. yield of monomethylaniline. Experiments in sealed tubes confirmed these results.

We have also investigated a variation of the above method, in which aniline hydrochloride and methyl alcohol are heated together in the presence of glacial acetic acid (*Ber.*, 1897, **30**, 3072). The most favourable result was a yield of 56 per cent. of methylaniline.

(3) The demethylation of dimethylaniline by heating with aniline hydrochloride at above 180°. In the most favourable experiments, a yield of 55 per cent. of methylaniline was obtained. Aniline was also heated to a high temperature with dimethylaniline hydrochloride with similar results, but it was found necessary to heat for a much longer period. This was probably due to the more basic nature of dimethylaniline. A condition of equilibrium between the three bases and hydrochloric acid would appear to be established.

At the time these experiments on demethylation were performed (1916), we were unable to find any record of similar work on this subject, apart from the well-known phenomenon of the transfer at above 300° of alkyl groups from nitrogen to the ring.

According to Schultz ("Chemie des Steinkohlentheers," 1900, 3rd ed., I, p. 98), monoethylaniline may be prepared by heating aniline hydrochloride with diethylaniline. No yields or references to the original literature are given, but the reaction is obviously not quantitative, since it is stated that the hydrochloride of diethylaniline remains in solution.

EXPERIMENTAL.

Preparation of Monomethylaniline according to D.R.-P. 75854.

Materials Used.—One hundred grams of aniline, 80·5 grams of formaldehyde (37 per cent.), 30 grams of methyl alcohol, 25 grams of sodium hydroxide solution (D 1·38), 150 grams of zinc dust, 1 litre of water, and 225 grams of sodium hydroxide solution.

* The published statements concerning the yields of monomethylaniline obtained in this way are very contradictory. See Wahl–Atack, "Organic Dyestuffs," p. 70; Cain, "Intermediate Products," p. 61; Lunge, "Chem. Techn. Untersuchungsmethoden," Vol. III., p. 761; Friedländer, "Fortschritte der Teerfarbenfabrikation," 1877—1887, p. 6.

The first four ingredients were mixed in a wide-mouthed bottle fitted with a stirrer and a reflux condenser, the zinc dust and water then added, and the temperature raised to about 90°. The remainder of the sodium hydroxide solution was gradually introduced and the stirring continued at this temperature until, after about twelve to fifteen hours, the methyleneaniline had disappeared. The bases were then distilled in a current of steam, extracted with ether, and a portion converted into the nitrosoamine. Yield of bases, 102 grams. Theory = 115 grams.

Thirty grams of the mixture gave 23 grams of dry phenylmethyl-nitrosoamine, whence the total yield of monomethylaniline is 54·5 per cent. of the theoretical.

Preparation of Monomethylaniline according to French Patent 212506.

In these experiments, the quantities of material and method of procedure were as described above, with the exception that the whole of the sodium hydroxide solution was added at once.

In one case, where particularly efficient stirring was employed, the methyleneaniline had disappeared in six and a-half hours. In this experiment, the mixed bases contained 65 per cent. of mono-methylaniline (by the nitrosoamine method of analysis), corresponding with a yield of 51·5 per cent. Other experiments with the same quantities and under similar conditions gave yields of 41·5 and 53·5 per cent. of the theoretical quantity of monomethyl-aniline.

Reduction in the Presence of Excess of Formaldehyde.

In two experiments on 100 grams of aniline, in which 0·5 molecular proportion of formaldehyde was used in excess, the yields of monomethylaniline were 46·5 and 55 per cent. In the first case, about 17 grams of the hydrochloride of p-nitrosodimethylaniline were obtained on nitrosification.

With an excess of 9 molecular proportions of formaldehyde, two experiments according to the German Patent gave scarcely any monomethylaniline; the reactions proceeded very slowly, and in one case much dimethylaniline was produced.

Reduction in Concentrated Alcoholic Solution.

One hundred grams of aniline, 25 grams of formaldehyde (36 per cent.), 840 grams of alcohol, 88 grams of solid sodium hydr-

oxide, 25 grams of aqueous sodium hydroxide (D 1·38), and 150 grams of zinc dust were vigorously stirred together. The reaction was complete in seven and a-half hours at about 60°, and the yield of methylaniline was 46·5 per cent. of the theoretical.

Reduction of s-Diphenylmethylenediamine.

Thirty grams of s-diphenylmethylenediamine, 125 grams of sodium hydroxide solution (D 1·38), 75 grams of zinc dust, 500 c.c. of water, and 25 grams of alcohol were mixed and vigorously stirred for ten and a-half hours at 70—90°. When a portion dissolved to a clear solution in dilute acetic acid (in which s-diphenylmethylenediamine is but sparingly soluble), the products were distilled in a current of steam.

Twenty-two grams of mixed bases were obtained, which gave 13 grams of phenylmethylnitrosoamine, corresponding with a yield of 10·2 grams of monomethylaniline. From the diazonium chloride solution, 10 grams of phenol were isolated, corresponding with 10 grams of aniline.

Reduction of the Condensation Product of Formaldehyde and Monomethylaniline.

Fifty grams of monomethylaniline, 19 grams of formaldehyde (36 per cent.), and 5—10 c.c. of aqueous sodium hydroxide were mixed, well shaken, and allowed to remain overnight.

The condensation product was separated by extraction with ether and reduced with a mixture of 150 grams of zinc dust, 1000 c.c. of water, 60 grams of methyl alcohol, and excess of sodium hydroxide solution at about 80°. After one and a-half days, the bases (44 grams) were removed by steam distillation. Nitrosification showed the product to contain 35 grams of monomethylaniline, whilst 9 grams of p-nitrosodimethylaniline hydrochloride were obtained.

The Interaction of Aniline Hydrochloride and Methyl Alcohol in an Autoclave and in Sealed Tubes.

In these experiments, the methylaniline was determined as the nitrosoamine and the aniline as phenol after decomposition of the diazonium salt. Dimethylaniline was separated and weighed as p-nitrosodimethylaniline hydrochloride, but as some of this always remained in solution, the figures for the tertiary base are low.

In experiment 8, aniline (140 grams) and sulphuric acid (16 grams) were used instead of aniline hydrochloride. Experiments 9—13 were made in sealed tubes, and in Nos. 11, 12, and 13 acetic acid (12 grams) was added.

Experi- ment.	Aniline hydro- chloride.	Methyl alcohol.	Tempera- ture.	Time in hours.	Percentage yield		
					Aniline.	Methyl- aniline.	Dimethyl aniline.
1	110	32	180°	$2\frac{1}{2}$	—	48·0	—
2	110	32	180	$2\frac{1}{2}$	27·0	51·5	—
3	110	32	180	$2\frac{1}{2}$	25·5	53·0	16·5
4	220	64	180	$2\frac{1}{2}$	36·0	52·0	7·0
5	220	64	190 above	$5\frac{1}{2}$	34·0	55·0	7·0
6	220	64	180	$4\frac{1}{2}$	26·0	53·0	10·0
7	220	96	180	3	—	45·0	20·0
8	140	84	190	$4\frac{1}{2}$	32·0	40·5	16·0
9	22	6·4	180	3	19·0	58·0	11·0
10	22	7·0	175	6	13·0	54·0	13·0
11	22	6·4	170	5	—	56·0	—
12	22	6·4	225	3	—	41·0	—
13	22	6·4	220	3	—	47·5	—

Methylation of Aniline under other Conditions.

(1) Twenty-six grams of aniline hydrochloride, 7 grams of methyl alcohol, and 25 c.c. of hydrochloric acid were heated in a sealed tube for six hours at 200—210°. Nitrosoamine = 13·5 grams; yield of methylaniline = 49·5 per cent.

(2) Thirty-six grams of aniline zincichloride and 6·4 grams of methyl alcohol were heated in a sealed tube for seven hours at 180°. Nitrosoamine = 7·5 grams; yield of methylaniline = 28 per cent.

(3) Twenty-two grams of aniline hydrochloride, 6·4 grams of methyl alcohol, and 15 grams of anhydrous calcium chloride were heated at 160° for three hours. Nitrosoamine = 10 grams; yield of methylaniline = 43 per cent.

(4 and 5). Twenty-eight grams of aniline (in the presence of 0·2 gram of iodine) were heated in one case with 10 grams, in another with 6·5 grams, of methyl alcohol for nine hours at about 220° (Knoll and Co., D.R.-P. 250236). In both cases, nitroso-amine = 15 grams. Yield of methylaniline = 42 per cent.

The Demethylation of Dimethylaniline.

First Series.—Interaction between aniline hydrochloride (13·0 grams) and dimethylaniline (12·0 grams) in molecular proportions in sealed tubes.

Experiment.	Temperature.	Time in hours.	Nitroso-amine.	Percentage yield of monomethylaniline
1	180°	6	12·5	46
2	200	6	15·0	55
3	230—235	5½	15·0	55

Second Series.—Interaction between dimethylaniline hydrochloride (31·5 grams) and aniline (18·6 grams) in molecular proportions in sealed tubes.*

Experiment.	Temperature.	Time in hours.	Nitroso-amine.	Percentage yield of monomethylaniline
1	180°	3	4	14·5
2	180	6	11·5	21·0
3[1]	200	13	28·0	51·0

[1] In Experiment 3 about 5 grams of a white solid separated on diluting the contents of the tube. This melted indefinitely at 144°, and after crystallisation from light petroleum indefinitely at about 160°. It was only superficially examined, and appeared to be a tertiary halogen-free base, possibly containing methyl groups in the benzene nucleus.

When 12 grams of dimethylaniline and 9·5 grams of aniline (molecular proportions) were heated for three hours at 220°, practically no monomethylaniline was produced.

Demethylation was found to occur when the two hydrochlorides were heated for three hours at 180°; thus, 13 grams of aniline hydrochloride and 15·8 grams of dimethylaniline hydrochloride (molecular proportions) gave 5·5 grams of the nitrosoamine, corresponding with a 20 per cent. yield of monomethylaniline.

The Separation of Aniline and Monomethylaniline using Zinc Chloride.

A mixture of aniline and monomethylaniline was treated with an aqueous solution of anhydrous zinc chloride. The precipitate was collected and thoroughly washed with light petroleum. After evaporation of the solvent, the residue of crude methylaniline was weighed and converted into the nitroso-derivative, which was removed from the mixture by extracting three times with ether, dried, and weighed.

The acid liquid which remained after the removal of the nitrosoamine, and contained traces of benzenediazonium chloride, was heated, saturated with salt, the phenol extracted with ether, and finally weighed. The aqueous filtrate from the zincichloride precipitate contained practically no aniline or methylaniline hydrochlorides.

* In Experiment 1 half these quantities were employed.

The accuracy of this method was checked by regeneration of the aniline from a given weight of the zincichloride

Analytical Results.—Taken: Aniline 20 grams, methylaniline 20 grams, fused zinc chloride 22 grams, water 50 c.c.

Obtained: Zincichloride, 37 grams, whence aniline = 19·2 grams. Phenylmethylnitrosoamine, 23·7 grams, whence methylaniline = 18·7 grams. Phenol, 0·25 gram, whence aniline = 0·25 gram.

There was also obtained 0·5 gram of bases from the aqueous filtrate from the zincichloride.

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XXIV.—*Equilibria in the Reduction of Oxides by Carbon.*

By Roland Edgar Slade and Geoffrey Isherwood Higson.

Equilibria of some reactions of the type:

metal oxide + carbon $\rightleftharpoons$ carbon monoxide + metal

or

metal oxide + metal carbide $\rightleftharpoons$ carbon monoxide + metal
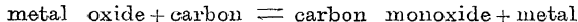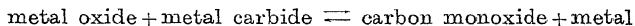
have been investigated.

In either of the above systems there are three components, namely, metal, carbon, and oxygen, and four phases, namely, metal, metal oxide, carbon (or carbide), and carbon monoxide (gas). The number of degrees of freedom is thus $3 + 2 - 4 = 1$. Therefore at one temperature there is one pressure of carbon monoxide which determines the equilibrium of the system   .

The following experimental method was adopted. A small quantity of the metal was heated in a vacuum to a certain temperature, and carbon monoxide was then admitted until the pressure was greater than the equilibrium pressure. The reaction proceeded in the direction from right to left, and carbon monoxide was absorbed until the equilibrium pressure was attained. Some carbon monoxide was then removed, when the reaction proceeded from left to right until the equilibrium pressure was again attained. If the carbon formed in the first part of the experiment did not remain as a separate phase either as a carbon or as a carbide, but formed a solid solution with the metal, there would be only two solid phases present with the gas phase; the system would there-

K*

fore have two degrees of freedom, and the pressure of carbon mon-
oxide would depend on the relative amounts of metal and carbon
present, as well as on the temperature. When the equilibrium
was attained from left to right, there was less carbon monoxide
present than when the equilibrium was attained from right to left,
therefore the equilibrium pressures would have been different in
these two cases if there were only two solid phases present.

The equilibrium may be calculated from the heat of reaction by
making use of the Nernst heat theorem. In the reaction

$$M + CO \rightleftharpoons MO + C + Q_t \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where M is the weight in grams of any metal combining with
16 grams of oxygen, and Q_t is the heat of reaction; in all cases
Q_t is positive, so that increase in temperature will cause the form-
ation of $M + CO$. That is to say, p_{co} increases with the tempera-
ture. This quantity of heat, Q_t, may be considered as the differ-
ences of two quantities of heat, Q_1 and Q_2, for if we write

$$M + O = MO + Q_1 \quad . \quad . \quad . \quad . \quad . \quad (2)$$
$$CO = C + O + Q_2 \quad . \quad . \quad . \quad . \quad . \quad (3)$$

then, on addition, $M + CO = MO + C + (Q_1 + Q_2)$. Q_2, the heat of
dissociation of carbon monoxide, is $-29,000$ calories, therefore

$$Q_t = Q_1 - 29,000 \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Neglecting terms containing T^2, the Nernst heat theorem requires
that

$$\log p_{co} = \frac{-Q_0}{4 \cdot 571 \, T} + 1 \cdot 75 \log T + 2 \cdot 6 \qquad (5)$$

where Q_0 is the heat of reaction at absolute zero.

The thermodynamic constant used for carbon monoxide is the
value given by Weigert in Abegg's "Handbuch." The relation
between Q_0 and Q_t is given by the equation

$$Q_0 = Q_t + 3 \cdot 5 \, T \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Limits of the Investigation.—The equilibrium mentioned above
could only be determined at temperatures at which the
equilibrium,

$$2CO \rightleftharpoons CO_2 + C,$$
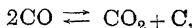
is practically completely in the left-hand direction. Rhead and
Wheeler (T., 1910, **97**, 2187; 1911, **99**, 1140) have investigated
this equilibrium, and from their results it is possible to calculate
the partial pressure of carbon dioxide in equilibrium with carbon
monoxide at 760 mm. or 50 mm. These values are given in
table I.

TABLE I.

Temperature.	Pressure of carbon dioxide in mm. when pressure of carbon monoxide is 760 mm.	Pressure of carbon dioxide in mm. when pressure of carbon monoxide is 50 mm.
850°	53·8	0·23
900	17·6	0·076
1000	4·6	0·0020
1100	0·90	0·00082
1200	0·46	0·00020

From these figures, it is seen that if the equilibrium pressure is as low as 50 mm., there is no complication due to the presence of carbon dioxide at temperatures from 850° upwards. If, however, the pressure is as great as 760 mm., the amount of carbon dioxide present is appreciable up to 1200°. If a carbide is present instead of free carbon, the ratio of carbon dioxide to carbon monoxide will be greater, for we have

$$\frac{p^2_{CO}}{p_{CO_2}p_c} = K,$$

and p_c (partial pressure of carbon vapour) will be lower over a carbide than over carbon.

In all our experiments, the equilibrium pressures were sufficiently low and the temperature was sufficiently high for the pressure of carbon dioxide to be negligible.

The metals with which we could determine the above equilibrium were only such as would fulfil the following conditions: (1) The metals must not be volatile at the temperature of the experiments. At these temperatures, the vapour pressure of the metal should certainly not be more than 0·25 mm., or it will distil rapidly on to parts of the platinum tube which are at a somewhat lower temperature, and probably attack the platinum. Platinum tubes were, in fact, destroyed by the volatility of boron and manganese. (2) The equilibrium pressure must not be greater than 50 mm. at 850°, or the quantity of carbon monoxide in the gas phase will be appreciable. (3) The equilibrium pressure must be sufficiently great to be measurable. It must be at least 1 mm. at 1300°. Applying the Nernst heat theorem to the equilibrium, we should only expect those elements of which the heat of oxidation, per gram-atom of oxygen, lies between 75,000 and 114,000 calories, to give an equilibrium pressure measurable in our apparatus. Of substances with known heats of oxidation, only silicon, boron, and manganese lie within this range. The only likely metals for which

the heats of oxidation were unknown, and which were readily obtainable, were vanadium, tantalum, and chromium.

Apparatus.—The furnace, which has been described by Slade (*Proc. Roy. Soc.*, 1912, [*A*], **87**, 519), consists of a platinum tube 2 cm. in diameter heated by a current of 300 to 400 amperes at 2 to 4 volts. The furnace is placed in a vessel which can be exhausted to prevent the platinum tube from collapsing under the pressure of the atmosphere. A silver capillary tube is used to connect the furnace with the glass tube leading to the pressure gauge. The temperatures were determined by means of a platinum platinum (90 per cent.)–rhodium (10 per cent.) thermocouple. The couple was calibrated up to the melting point of copper, 1083°, and higher temperatures were determined by extrapolating by means of the formula

$$\log e = 1\cdot 22 \log t - 2\cdot 65,$$

where t is expressed in degrees centigrade and e in millivolts. The cold end of the couple was kept at 0°.

It was found to be impossible to use a platinum boat for any of the substances investigated, for although the temperatures were well below their melting points, they were rapidly alloyed with platinum. Accordingly, boats of unglazed Royal Berlin porcelain were employed.

Pressures were read on a mercury vacuum manometer, behind which was a glass millimetre scale illuminated by a lamp and a milk-glass screen. The readings were made with a telescope, and were accurate to ±0·05 mm.

The carbon monoxide was prepared by running pure formic acid into concentrated sulphuric acid at 70—80°. The gas, which was first passed through a long tube of soda-lime and then through a similar tube of phosphoric oxide, was collected and stored over mercury in a vessel of 1 litre capacity.

The gas was led from the reservoir to the furnace and pressure gauge by means of a tube, in which were placed two taps separated by a capillary tube of such dimensions that the volume between the two taps was 0·2 c.c. By filling this tube with carbon monoxide at the ordinary temperature, then closing one tap and opening the other, 0·2 c.c. of carbon monoxide was allowed to flow into the exhausted furnace and the tubes connecting the furnace to the gauge and pump. The total volume of this part of the apparatus was about 50 c.c., and when the furnace was heated to about 1200°, its effective volume was about 30 c.c., so that the introduction of 0·2 c.c. under a pressure of one atmosphere caused a rise of pressure of $\frac{0\cdot 2}{30}$ atmosphere, or about 5 mm. of mercury.

In most of the experiments, 0·1 gram of the metal under investigation was introduced into the boat. That this was sufficient may be seen from the following considerations.

If the reaction is

$$M + CO = MO + C,$$
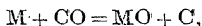
where M is two equivalents of an element, then two gram-equivalents of the element would react with 22,400 c.c. of carbon monoxide. If the pressure in the furnace was 60 mm., which was the maximum pressure used in several cases, the volume of gas contained in the furnace was 2·4 c.c. when measured at $N.T.P.$, therefore to absorb all this gas, $\frac{2\cdot4}{22,400} \times 2 = 2\cdot2 \times 10^{-4}$ gram-equivalent of the element would be required. If the equivalent were as great as 100, only 0·02 gram would be required. The metal was usually broken into small pieces, as the velocity of the action must be proportional to the surface exposed.

Experiments with Vanadium.—As vanadium is a very refractory substance and is difficultly reducible (that is, the oxide has a high heat of formation), it was decided to attempt to measure the reduction equilibrium.

Some preliminary experiments were made on the action of vanadium on platinum and the melting point of vanadium. The vanadium was placed, in very small pieces (about 0·5 mm. in diameter and less), on a platinum strip which was heated in an atmosphere of hydrogen by an electric current. At 1400°, the vanadium adhered to the strip when the heating had been carried on for some three minutes. The temperature was determined by means of a Wanner pyrometer, correction being made for black-body radiation of the platinum. In another experiment, the strip was dusted with powdered vanadium and heated rapidly until it fused at one point. Examination under the microscope showed that the vanadium had then fused into globules just round the portion of the strip which had fused. The melting point of this vanadium is therefore just below the melting point of platinum, namely, 1760°. The vanadium had been prepared in the electric furnace, and contained 4·6 per cent. of carbon. The carbon probably exists as the carbide, VC, and may be present in solid solution, although the fact that so much carbon is present makes it seem probable that the carbide exists as a separate phase.

Experiments.—0·0636 Gram of the metal was placed in an unglazed porcelain boat in the platinum tube furnace. The furnace was exhausted and left for sixteen hours, when no rise of pressure was noticeable. The temperature was raised to 1000°, and the occluded gas from the boat pumped off; 0·2 c.c. of carbon mon-

oxide was then admitted, and this raised the pressure to 6 mm., at which it remained. Therefore the equilibrium pressure was greater than this, or the velocity of reaction at this temperature was very small. The latter was found to be the case, for when the pressure of carbon monoxide had been increased to 60 mm., there was still no reaction. The temperature was then raised to 1340°, and maintained at this temperature for four and a-half hours. During this time, the pressure fell at first rapidly, and finally became steady at 1·7 mm. The temperature was then reduced to 1145°, where it was maintained for thirty minutes. The pressure fell rapidly to 0·55 mm., where it remained constant. The temperature was then lowered to 900°, when the pressure fell only to 0·2 mm.

On the following day, the furnace was heated to 1340° and the temperature kept constant. In one hour the pressure rose to 1·2 mm., at which it remained constant for three and a-half hours.

The equilibrium pressure at 1340° was therefore between 1·7 and 1·2 mm. The mean of these values is 1·45 mm. At lower temperatures, the equilibrium was attained too slowly to be determined.

The reaction is probably

$$VO + VC \longrightarrow 2V + CO + Q.$$
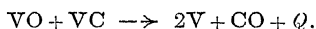
The value

$$p_{co} = \frac{1·45}{760} \text{ atm. at } 1340°$$

gives, by the Nernst heat theorem, the value

$$Q_0 = 80,875 \text{ cals.}$$

Substituting this in equation (5), we find that

$$p_{co} = 1 \text{ atmosphere at } 1827°.$$

This is the temperature at which vanadium oxide would be reduced by the carbide under a pressure of one atmosphere.

There is no direct evidence as to the heat of formation of vanadium carbide, that is, of the reaction

$$V + C \longrightarrow VC,$$

but usually the heats of formation of carbides are small (Wartenberg, *Zeitsch. anorg. Chem.*, 1907, **52**, 299), that is to say, not greater than 2000—3000 calories per gram-atom of carbon. If this heat of formation of the carbide is neglected, an approximate value of the heat of oxidation of vanadium at 20° can be obtained:

$$V + O = VO + 111,000 \text{ cals.}$$
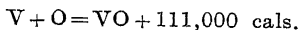
Not much trust can be placed in this value, however, for the carbide may be in solid solution in the metal and not as a separate phase.

Experiments with Tantalum.—The tantalum used was a portion of a specimen obtained from the late Dr. Werner von Bolton, and used by von Hevesy and Slade to determine the electrode potential of tantalum. It was in the form of a rolled sheet about 0·25 mm. thick. As only a small quantity of the metal was available, 0·035 gram was used in each experiment. If the tantalum was oxidised to the oxide, Ta_2O, this metal would absorb 3·5 c.c. of carbon monoxide. In the first experiment with tantalum, the metal was in the form of one piece of sheet. At 1000°, 2 c.c. of carbon monoxide were admitted ($p=60$ mm.); the pressure fell, and in two hours became constant at 0·7 mm. The temperature was then raised to 1200° and 0·6 c.c. of carbon monoxide was admitted, so that the pressure was raised to 14 mm. As the pressure did not fall, more carbon monoxide was admitted until the pressure was 40 mm., but there was still no action. The furnace was therefore exhausted, but no appreciable rise in pressure took place in two hours. It therefore seemed probable that the constant pressure of 0·7 mm. obtained at 1000° was not a true equilibrium pressure, but that the equilibrium pressure, even at 1200°, was very low indeed.

In the next experiment the same quantity of metal was used, but it was cut into as many strips as possible, in order to increase the surface. After pumping out all gases from the boat at 1150°, 0·4 c.c. of carbon monoxide was admitted, so as to raise the pressure to about 13 mm. In half an hour the pressure fell to 0·2 mm., and then became constant, and remained so for half an hour. An attempt was now made to reach the equilibrium from the low pressure side. The furnace was exhausted and the temperature was raised to 1270°. In four hours the pressure rose slightly above 0·1 mm. (perhaps 0·12 mm.), and remained constant for about three hours. Carbon monoxide (about 0·1 c.c.) was then admitted to raise the pressure to 2·5 mm., and in one hour the pressure fell to 0·1 mm. This value is therefore the equilibrium pressure at 1270°.

It was impossible to determine the equilibrium at a higher temperature, because at this stage of the work the platinum tube had become weakened and slowly collapsed when kept exhausted for several hours at 1270°, although the external pressure on the tube was only 30—40 mm. of mercury.

Experiments with Chromium.—The temperature of reduction of chromium sesquioxide was determined by Greenwood (T., 1908, **93**, 1438), who found that this oxide was reduced at 1195° under a

pressure of 2 mm. The boiling point of chromium is 2200° (Green-wood), and from this value the vapour pressure of liquid chromium can be calculated to be 0·07 mm. at 1000°, 0·078 mm. at 1100°, 0·7 mm. at 1200°, and 1·12 mm. at 1300°. It was therefore not safe to heat chromium to a much higher temperature than 1200° in the platinum furnace.

The chromium had been prepared by the Goldschmidt method, and therefore contained a trace of aluminium. As aluminium is easily and completely oxidised by carbon monoxide, it is probable that it would only have a very slight influence on the equilibrium.

0·45 Gram of metal, in the form of a coarse powder, was used in the first experiment. The furnace was heated to 936°, and all adsorbed gases were pumped out. Carbon monoxide was then admitted until the pressure was 100 mm. In nine and a-half hours the pressure fell to 22 mm., but did not appear to be approaching a steady value. After remaining for eighty-five hours, the furnace was heated to 1010° and carbon monoxide admitted until the pressure was 50 mm. In six hours the pressure fell to 0·75 mm., and appeared to be constant. After eighteen hours, the temperature was raised to 1292°, and carbon monoxide admitted until the pressure was 63 mm. In forty-five minutes the pressure fell to 6·2 mm., and remained constant. Carbon monoxide was then pumped out until the pressure fell to 5 mm. In fifteen minutes the pressure rose to 6·2 mm., and remained constant. The temperature was then raised to 1339°, and in twenty-five minutes the pressure had risen to 9·1 mm., and become constant. The furnace was then cooled, and next day was heated to 1339°. In twenty minutes the pressure rose to 9·2 mm. The furnace was now cooled to 1292°, and carbon monoxide was pumped off until the pressure was less than 1 mm. In an hour the pressure became constant at 4·4 mm. The furnace was cooled, and the next day was heated to 1292°; the pressure rose to 4·4 mm. Carbon monoxide was then admitted until the pressure was 8·6 mm. In forty-five minutes the pressure fell to 4·4 mm. The temperature was now raised to 1339°, when the pressure rose to 9·2 mm. In the figure are given some of the time—pressure curves obtained. These show how accurately the results could be reproduced.

A new sample of chromium (0·45 gram) was now introduced into the furnace, and the temperature was raised to 1292°, carbon monoxide being admitted until the pressure was 15 mm. In twenty minutes the pressure fell to 6·2 mm., and remained constant at this value for one hour. The temperature was then raised to 1339°, and the pressure rose to 9·1 mm., but the platinum tube began to leak, owing to its being attacked by the chromium, which had distilled on to it during this and former experiments.

Table II shows the values for the equilibrium pressure obtained with chromium. All these equilibrium pressures were obtained twice from each side. The high value at 1292° is the value obtained when the furnace had not been raised to a higher temperature. After the temperature had been raised to 1339° and lowered again to 1292°, the equilibrium pressure was 4·4 mm., and this value could be obtained again and again. Since chromium easily forms a carbide, it is probable that the reaction taking place was

$$5\,Cr + CO \; \rightleftharpoons \; Cr_4C + CrO + Q.$$

Time in hours.
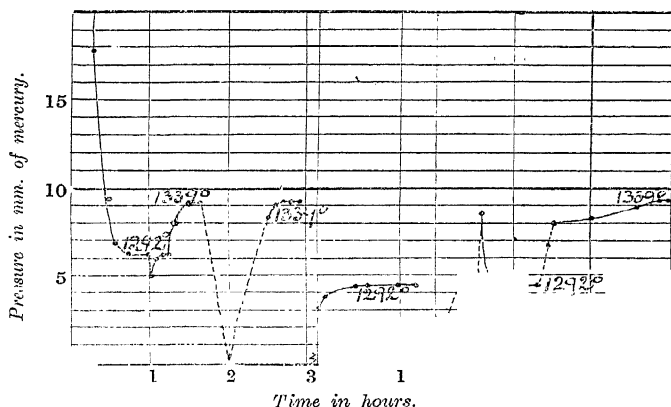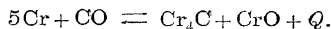
Calculating the heat of reaction per gram-atom of oxygen at 1315° from the Nernst formula and the van't Hoff formula, the values given in table II are obtained.

TABLE II.

Temperature.	Pressure of carbon monoxide in mm.	Q_t calculated, Nernst.	Q_t calculated, van't Hoff.
1292°	6·2	73,600	
1339	9·2	69,200 ⎫	77,000
1292	4·4	69,200 ⎭	

The value 77,000 calories is the heat of reaction calculated from the integrated form of the van't Hoff equation,

$$Q_t = -\,4\cdot571\,(\log p_2 - \log p_1)\frac{T_1 T_2}{T_2 - T_1}.$$

In this method of calculating Q_t, an error of 0·1 mm. in the determination of the equilibrium at 1292° would make a difference of a little more than 1000 calories in the value of Q_t. The assumption on which this formula is based, however, is only that the heat

of reaction does not change appreciably between the two temperatures. That two different values were obtained for the equilibrium at 1292°, according to whether the furnace had been heated up to 1339° or not, must be explained by supposing that the substances in equilibrium were different in the two cases. It is very improbable that the first value is due to the presence of a trace of aluminium in the metal, for the presence of aluminium would be expected to lower rather than to raise the equilibrium pressure, and in the two experiments in which the pressure was 6·2 mm., very different amounts of carbon monoxide had been absorbed by the same amount of metal. In the first experiment, 6—7 c.c. of carbon monoxide, and in the second case only 0·6 c.c., were absorbed.

The equilibrium in the gas phase is represented by

$$p_{co} \quad K . \frac{p_{carbide} \quad p_{oxide}}{}.$$

The change in the system caused by raising the temperature to 1339° was to give a lower equilibrium pressure at 1292°, and this must be due to (1) increase in the partial pressure of chromium, (2) lowering of the partial pressure of the carbide, or (3) lowering of the partial pressure of the oxide.

Case (1) might be caused by the existence of a transition point of chromium between 1292° and 1339°. At first, the metal is in the α-form, stable at lower temperatures; on heating, the metal would change to the other, or β-form, and on cooling to 1292° would not revert to the α-form, but remain in the unstable β-form, which would have a higher vapour pressure than the α-form.

Case (2) might be caused by the formation of an unstable carbide in the first instance, which on heating to 1339° changes into the stable form. On cooling now to the lower temperature, the unstable carbide is not formed in the presence of the more stable one.

Case (3) might be caused by the chromium oxide combining with the silica in the boat to form a silicate, but this reaction should not be different after the furnace had been raised to the higher temperature. The first explanation seems the more probable.

XXV.—*The Dissociation Pressures of some Nitrides.*

By Roland Edgar Slade and Geoffrey Isherwood Higson.

Equilibria of the type

$$2M + N_2 \rightleftharpoons 2MN,$$
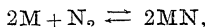
where M is three equivalents of a metal, have been investigated. In this system there are two components, namely, metal and nitrogen, and three phases, namely, metal, nitride, and nitrogen. The number of degrees of freedom is thus $2 + 2 - 3 = 1$, and therefore at one temperature there is one pressure of the nitrogen which determines the equilibrium of the dissociation. If the nitride dissolves in the metal as a solid solution, there are only two phases, and the number of degrees of freedom is therefore two. The equilibrium will then be determined, not only by the pressure of the nitrogen, but also by the composition of the solid phase.

Applying the Nernst heat theorem to the equilibrium

$$M + \tfrac{1}{2}N_2 = MN + Q,$$
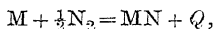
where Q is the heat evolved when half a gram-molecule of nitrogen combines with the metal, we have

$$\log p_{N_2} = -\frac{Q_0}{4 \cdot 571 T} + 1 \cdot 75 \log T + 2 \cdot 6$$

and

$$Q_t = Q_0 - 3 \cdot 5T,$$

where Q_0 and Q_t, respectively, are the heats of reaction at absolute zero and some other temperature, T. As the heats of formation of the nitrides investigated were unknown, it is impossible to apply these equations to determine the value of p_{N_2}, but it will be seen that the pressure of nitrogen at 1127° would be 1 mm. if the heat of formation of the nitride were 70,600 cals. and 60 mm. if the heat of formation were 59,000 cals.

Experimental.

The furnace used for the determination of the equilibria is described in the preceding paper.

Nitrogen was prepared by heating a solution containing ammonium chloride, potassium nitrate, and potassium dichromate. The dichromate served to oxidise any oxides of nitrogen to nitric acid, which was absorbed by passing the gas through a long tube of soda-lime. The nitrogen was then dried by passage through a long tube of phosphoric oxide.

The equilibria were determined by heating small quantities of

the metal to a known temperature, introducing nitrogen into the furnace, and determining the value to which the pressure fell. Nitrogen was then pumped out, and the equilibrium was determined from the low-pressure side.

Vanadium.—This metal is known to form two nitrides, VN and VN_2.

At 1203°, the equilibrium pressure was found to be slightly less than 0·2 mm., and at 1271° slightly less than 1·5 mm. The equilibrium pressure is somewhere near these values, but equilibrium was attained very slowly, and it was impossible to heat the platinum tube in use at that time to a higher temperature.

Boron.—An attempt was made to determine the dissociation pressure of boron nitride at 1100° and 1240°.

At 1100°, the velocity was too low for the equilibrium to be determined. At 1240°, the pressure of nitrogen fell from 26·4 mm. to 9·4 mm. in six hours, and appeared to be approaching the constant value of about 9 mm., but the boron attacked the platinum tube and caused it to leak, so that further experiments could not be made.

Tantalum.—Tantalum is known to form two stable nitrides, TaN and Ta_3N_5. In our experiments, it is probable that the lower nitride, TaN, was formed.

When the metal was heated at 1170° in nitrogen under 15 mm. pressure, the gas was slowly absorbed until the pressure fell to 0·5 mm. The furnace was then exhausted to 0·05 mm. The pressure rose in two hours to 0·4 mm.

In another experiment, at 1308°, the pressure fell from 9 mm. to 1·2 mm. in one and a-half hours, and remained constant for half an hour. The furnace was then allowed to cool. Next day it was completely exhausted, and again heated to 1308°. The pressure rose to 0·8 mm., and remained constant at this value for two hours.

Summary of Results.

	Tempera-ture.	Pressure of nitrogen.	Heat of formation of nitride, that is, Q_0, calculated from Nernst's formula.
Vanadium	1203°	Not greater than 0·2 mm.	79,200 cals.
	1271	,, ,, 1·5 ,,	77,200 ,,
Boron ...	1222	,, ,, 9·4 ,,	About 69,000 ,,
Tantalum	1170	0·4—0·5 mm.	74,700—75,500 cals.
	1308	0·8—1·2	79,900—82,800 ,,

This investigation was carried out in the Muspratt Laboratory of Physical Chemistry, University of Liverpool.

XXVI.—*Nitro-, Arylazo-, and Amino-glyoxalines.*

By ROBERT GEORGE FARGHER and FRANK LEE PYMAN.

THIS investigation was begun with the object of effecting the synthesis of purine derivatives by a method complementary to those which have been employed hitherto. In these, the pyrimidine nucleus is first built up and the glyoxaline ring closed subsequently. We proposed to prepare 4-aminoglyoxaline-5-carboxylic acid,* condense it with cyanic acid, and eliminate water with the production of xanthine.

$$\begin{array}{ccc} \underset{\text{NH}_2 \cdot \text{C---N}}{\text{CO}_2\text{H} \cdot \text{C} \cdot \text{NH}} \!\!>\!\!\text{CH} & \underset{\text{NH--C- -N}}{\overset{\text{NH}_2 \ \ \text{CO}_2\text{H}}{\underset{}{\text{CO} \ \ \text{C} \cdot \text{NH}}}} \!\!>\!\!\text{CH} & \underset{\text{NH-C---N}}{\overset{\text{NH--CO}}{\text{CO} \ \ \text{C} \cdot \text{NH}}} \!\!>\!\!\text{CH.} \end{array} \longrightarrow$$
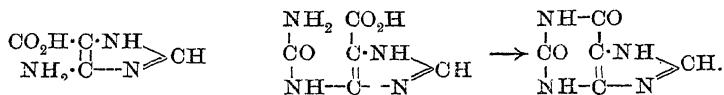
Such a synthesis would be of interest in view of the suggestion that purine derivatives originate from histidine in the animal body (compare Hopkins, T., 1916, **109**, 629).

Although the starting material for the proposed synthesis, 4-aminoglyoxaline-5-carboxylic acid, was unknown, we did not anticipate that its preparation would offer any serious difficulty. We have, however, so far failed to obtain this substance, and now give an account of our attempts to prepare this and other amino-substituted glyoxalines.

An account of the investigation may be subdivided under three headings: first, the preparation of the glyoxalines and their carboxylic acids, which were required as starting materials; second, the preparation and properties of nitroglyoxalines; and last, the preparation and properties of arylazoglyoxalines.

(1) *The Preparation of Glyoxalines and their Carboxylic Acids.* —For the purpose of this investigation, it was necessary to prepare considerable quantities of glyoxaline-4:5-dicarboxylic acid, the most convenient source of glyoxaline. This acid was first prepared by Maquenne (*Ann. chim. phys.*, 1891, [vi], **24**, 525), by mixing aqueous solutions of nitrotartaric acid and hexamethylenetetramine, adding ammonia, and allowing the mixture to become hot, and subsequently by Dedichen (*Ber.*, 1906, **39**, 1835), who replaced the hexamethylenetetramine by formaldehyde. We have carried out a large number of experiments on the best conditions for the pre-

* In glyoxalines containing a free imino-group, the 4- and 5-positions are equivalent.

paration of this acid, and find that to obtain a good yield it is essential that the reaction mixture should be kept cold.

A number of experiments were carried out with the object of effecting the partial decarboxylation of glyoxaline-4:5-dicarboxylic acid, and thus producing glyoxaline-4-carboxylic acid by a more convenient and economical process than that previously employed, where six operations are required in its synthesis from citric acid through 4-hydroxymethylglyoxaline (T., 1911, **99**, 668; 1916, **109**, 186). When the acid is heated with water, 10 per cent. hydrochloric acid, or concentrated hydrochloric acid, little decarboxylation takes place below 180°, but above this temperature, the action proceeds more readily, glyoxaline being the main product, whilst a small proportion of glyoxaline-4-carboxylic acid can be isolated provided that the heating has not been too prolonged. When the acid is heated with an excess of concentrated ammonia at 180° to 200°, the main product is glyoxaline,* and a similar result is obtained by heating the aqueous solution of the mono-sodium salt.

The desired result can be obtained, however, by boiling the acid with aniline, when the *anilide* of glyoxaline-4-carboxylic acid is formed in a yield amounting to 45 per cent. of the theoretical. From this, the acid is readily prepared by hydrolysis.

$$CO_2H \cdot C \cdot NH$$
$$CO_2H \cdot C --- N$$

$$PhNH \cdot CO \cdot C \quad \begin{matrix} CH \cdot NH \\ --- N \end{matrix} \!\!> CH$$

$$CO_2H \cdot C \quad \begin{matrix} CH \cdot NH \\ --- N \end{matrix} \!\!> CH.$$
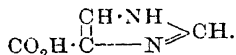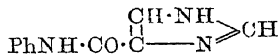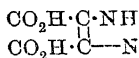
For the purpose of orientation, it was necessary to prepare glyoxalines substituted in the 2-, 4:5-, and 2:4:5-positions. The 2-alkylglyoxalines were prepared by suitable modifications of Maquenne's methods. From 2-methylglyoxaline-4:5-dicarboxylic acid, *2-methylglyoxaline-4-carboxylic acid* was obtained through its *anilide*.

As representatives of 4:5- and 2:4:5-substituted glyoxalines, 4:5-dimethylglyoxaline and 2:4:5-trimethylglyoxaline were prepared by modification of known methods.

(2) *Nitroglyoxalines.*—The nitration of various glyoxalines has led to the formation of mononitroglyoxalines in the hands of several observers. In some cases the nitro-group evidently enters the 4-(or 5-)position, since no other position is vacant; for instance, in the nitration of 2-methylthiol-1-phenyl(and 1-methyl)glyoxaline

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* We were unable to find any evidence of the formation of the imide of glyoxaline-4:5-dicarboxylic acid, from which the desired 5-aminoglyoxaline-4-carboxylic acid might have been obtained by the action of hypobromous acid.

(I) (Wohl and Marckwald, *Ber.*, 1888, **22**, 568, 1353) and 2:4-di-methylglyoxaline (II) (Windaus, *Ber.*, 1909, **42**, 758):

$$\begin{array}{l} \text{CH·NR} \\ \text{||} \quad\quad \text{>C·SMe} \\ \text{CH — N} \end{array} \qquad\qquad \begin{array}{l} \text{CH·NH} \\ \text{||} \quad\quad \text{>CMe.} \\ \text{CMe— N} \end{array}$$

        (I.)   (II.)
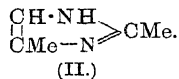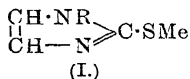
The orientation of the nitro-group in nitroglyoxaline itself (Rung and M. Behrend, *Annalen*, 1892, **271**, 28; R. Behrend and Schmitz, *ibid.*, 1893, **277**, 338) and in nitro-4-methylglyoxaline has not been determined previously, but an indication that the latter contains the nitro-group in the 5-position is afforded by Windaus's observation (*loc. cit.*) of its close similarity to 5-nitro-2:4-dimethyl-glyoxaline.

Moreover, whilst *4-nitro-2-methylglyoxaline* is readily prepared, we were unable to obtain a nitro-derivative of 4:5-dimethyl-glyoxaline, for in this case part of the base was completely oxidised, whilst a considerable proportion remained unchanged, and the only isolable derivative was the nitrate of 4-methylglyoxaline-5-carb-oxylic acid, which has been described by Gerngross (*Ber.*, 1912, **45**, 509).

The inability of a glyoxaline substituted in both the 4- and 5-positions to form a nitro-derivative indicates that the nitro-glyoxalines contain the substituent in the 4-(or 5-)position. This view is confirmed by their behaviour on reduction. Wohl and Marckwald (*loc. cit.*) attempted to reduce the 4-(or 5-)nitro-2-methylthiol-1-phenyl-(and 1-methyl)glyoxalines to the correspond-ing amines, but obtained only decomposition products, including methyl mercaptan. Similarly, we find that 4-nitro-2-methyl-glyoxaline undergoes fission on reduction with tin and hydrochloric acid, two of the three atoms of nitrogen in the molecule appearing in the form of ammonia.*   Since precisely the same result is obtained with nitroglyoxaline and nitro-4-methylglyoxaline, whilst it is shown below that 2-aminoglyoxalines are stable, it is clear that these nitro-derivatives are 4-nitroglyoxaline and 5-nitro-4-methyl-glyoxaline respectively.

Before we had arrived at this conclusion, we were anxious to prepare some of the nitroglyoxaline-4-carboxylic acid, which Windaus and Opitz (*Ber.*, 1911, **44**, 1721) obtained by the action of boiling 25 per cent. nitric acid on 4-β-hydroxyethylglyoxaline.

* The first stage in the disintegration of the 4-aminoglyoxalines is probably the elimination of the amino-group as ammonia, with the formation of a glyoxalone, for certain members of the purine group—also derivatives of 4-aminoglyoxaline—have been shown to undergo hydrolysis in this manner (compare, for instance, Tafel and Mayer, *Ber.*, 1908, **41**, 2546; Biltz, *Ber.*, 1910, **43**, 1589).

These authors state that the yield of 4-β-hydroxyethylglyoxaline, obtained by the action of barium nitrite on 4-β-aminoethyl-glyoxaline hydrochloride, was so poor that the nitro-compound was not available in sufficient quantity for further study. It appeared to us, however, that this nitro-compound might be obtained by the action of nitric acid on other more readily accessible derivatives of glyoxaline containing a side-chain of carbon atoms in the 4-position, and in the first place we employed compounds containing two carbon atoms in the side-chains, like Windaus's starting material. The results were disappointing; 4-β-aminoethyl-glyoxaline, when boiled with 50 per cent. nitric acid for nine hours, was mainly recovered unchanged, whilst 4-cyanomethyl-glyoxaline was converted under the same conditions almost quantitatively into glyoxaline-4-acetic acid. Attempts to nitrate glyoxaline-4-carboxylic acid and glyoxaline-4:5-dicarboxylic acid were likewise unsuccessful. The prospect of nitrating 4-hydroxy-methylglyoxaline was not hopeful, for it has been shown previously (T., 1916, **109**, 186) that hot concentrated nitric acid converts it into glyoxaline-4-formaldehyde and glyoxaline-4-carboxylic acid. It has now been found that the alcohol gives the same products when digested on the water-bath with fuming nitric acid, whilst it can be recovered almost quantitatively after boiling with ten parts of 25 per cent. nitric acid for four hours. On the other hand, the nitration of 4-hydroxymethylglyoxaline with nitric and sulphuric acids gave rise to a product which was not obtained in crystalline form, but further study of this was omitted in view of the peculiar behaviour of the simple nitroglyoxalines on reduction.

(3) *Arylazoglyoxalines.*—The constitution of the arylazo-derivatives of simple glyoxalines has not been settled hitherto. Rung and Behrend (*Annalen*, 1892, **271**, 28), who first isolated benzene-azoglyoxaline, considered it to be a diazoimino-compound (I), because boiling acids decomposed it with the formation of nitrogen

$$\begin{array}{c} \text{CH·N(N:NPh)} \\ | \qquad\qquad \searrow\!\text{CH,} \\ \text{CH}\!\!-\!\!-\!\!-\!\!-\!\!\text{N} \end{array}$$

(I.)
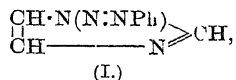
and glyoxaline. Burian (*Ber.*, 1904, **37**, 696), who prepared many arylazoglyoxalines from diazobenzene-*p*-sulphonic acid and various glyoxalines, adopted the same view of the constitution of these compounds on other grounds, namely, because all the glyoxalines substituted in some or all of the 2-, 4-, and 5-positions which he examined coupled with the diazonium salt, whilst 1-substituted glyoxalines did not. Pauly (*Zeitsch. physiol. Chem.*, 1904, **42**, 508), however, pointed out the possibility that the arylazo-

glyoxalines were true C-azo-compounds (II) similar to those obtained from pyrrole, and later (*ibid.*, 1915, **94**, 284) attributed the probable formula (III) given below to the compound obtained by the action of diazotised arsanilic acid on histidine, owing to its stability towards acids. Whilst in the case of these simple

$$\underset{\text{(II.)}}{\overset{\displaystyle ArN:N\cdot C\cdot NH}{\underset{\displaystyle CH\cdot N}{\big|\big|}}}\!\!\!\!>\!\!CH$$

$$\underset{\text{(III.)}}{\overset{\displaystyle AsO_3H_2\cdot C_6H_4\cdot N:N\cdot C\cdot NH}{\underset{\displaystyle CO_2H\cdot CH(NH_2)\cdot CH_2\cdot C\!-\!-\!N}{\big|\big|}}}\!\!\!\!>\!\!C\cdot N:N\cdot C_6H_4\cdot AsO_3H_2$$
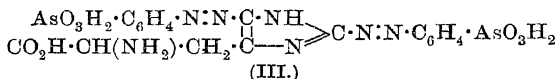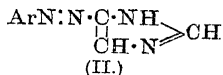
glyoxalines the orientation of the arylazo-group is uncertain, the constitution of the arylazopurines is known, for Hans Fischer (*Zeitsch. physiol. Chem.*, 1909, **60**, 69) has shown that the arylazo-group enters the 8-position of the purine nucleus—the 2-position of its glyoxaline ring—by reducing arylazopurines to 8-aminopurines.

In view of this result, it appeared to us probable that the arylazo-derivatives of simple glyoxalines were also C-azo-compounds, as Pauly suggested, and it was of interest to determine whether the arylazo-group entered the 2- or the 4-position, and the nature of the products obtained on reduction.

The benzeneazoglyoxaline of Rung and Behrend was first examined. By the method of these workers, it is obtained in poor yield, but by the action of benzenediazonium chloride on one molecular proportion of glyoxaline in an excess of aqueous sodium carbonate, it is readily obtained mixed with a little $2:4:5\text{-}tris\text{-}$ *benzeneazoglyoxaline*. 2-Benzeneazoglyoxaline melts at 190° (corr.), and it is therefore evident that the specimen prepared by Rung and Behrend, melting at 177—178°, was impure. The pure substance is reasonably stable towards boiling 10 per cent. hydrochloric acid, for a considerable proportion can be recovered unchanged after two hours.

The constitution of 2-benzeneazoglyoxaline (IV) was proved by reduction. With zinc dust and hot acetic acid, it yields aniline and glycocyamidine * (V), the formation of the latter showing that the benzeneazo-group is attached to the 2-position of the ring.

$$\underset{\text{(IV.)}}{\overset{\displaystyle CH\cdot NH}{\underset{\displaystyle CH\!-\!-\!N}{\big|\big|}}}\!\!\!\!>\!\!C\cdot N:NPh \qquad\qquad \underset{\text{(V.)}}{\overset{\displaystyle CH_2\cdot NH}{\underset{\displaystyle CO\!-\!-\!NH}{}}}\!\!\!\!>\!\!C:NH + PhNH_2$$
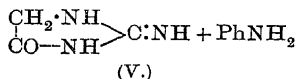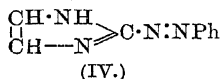
* The conversion of glyoxaline into glycocyamidine and 2-aminoglyoxaline, both derivatives of guanidine, is of biochemical interest, firstly, because creatinine is the N-methyl derivative of glycocyamidine, and secondly, on account of the similar behaviour of histidine and arginine in purine metabolism (compare Hopkins, *loc. cit.*).

This result is confirmed by the formation of a small amount of guanidine on the reduction of 2-benzeneazoglyoxaline with stannous chloride. In this reduction, a small quantity of 2-*aminoglyoxaline* is formed and some aniline, but the main product is 2-*amino*-4-p-*aminophenylglyoxaline* (VI), a compound resulting from a change of the benzidine type. It is also formed in small proportion in the reduction with zinc dust and acetic acid.

$$NH_2 \cdot C_6H_4 \cdot C \underset{\substack{|| \\ CH \cdot NH}}{\overset{}{\text{---}}} N \!\!\! > \!\!\! C \cdot NH_2$$
(VI.)

$$C_6H_5 \cdot NH \cdot C \underset{\substack{|| \\ CH \cdot NH}}{\overset{}{}} \text{---} N \!\!\! > \!\!\! C \cdot NH_2$$
(VII.)

$$CH \underset{\substack{|| \\ CH \cdot NH}}{\overset{}{\text{---}}} N \!\!\! > \!\!\! C \cdot NH \cdot C_6H_4 \cdot NH_2$$
(VIII.)

Its constitution was proved by the oxidation of its diacetyl derivative with potassium permanganate, when *p*-acetylaminobenzoic acid was formed. This result eliminated the possibility that the compound had one of the two formulæ (VII) or (VIII), representing substances formed by a change of the semidine type. The occurrence of a rearrangement of the benzidine type in a five-membered heterocyclic nucleus seems remarkable at first sight, but a closer inspection of the formula shows that the conjugated system connecting the 2- and 5-carbon atoms of the glyoxaline ring is similar to that existing in the benzene nucleus.

Whilst no other case of the benzidine type of change in a heterocyclic nucleus has been observed previously, so far as we are aware, Michaelis and Schäfer (*Annalen*, 1915, **407**, 229) have obtained by the reduction of 1-phenyl-3-methyl-4-benzeneazo-pyrazole (IX) the two isomerides (X) and (XI) which result from the two possible changes of the semidine type.

$$\underset{(IX.)}{\overset{\displaystyle NPh}{\underset{\substack{N \quad\; CH \\ || \qquad || \\ CMe \cdot C \cdot N : NPh}}{}}}$$
$$\underset{(X.)}{\overset{\displaystyle NPh}{\underset{\substack{N \quad\; C \cdot NHPh \\ || \qquad || \\ CMe \cdot C \cdot NH_2}}{}}}$$
and
$$\underset{(XI.)}{\overset{\displaystyle NPh}{\underset{\substack{N \quad\; CH \\ || \qquad || \\ CMe \cdot C \cdot NH \cdot C_6H_4 \cdot NH_2}}{}}}$$

Owing to the formation of 2-amino-4-*p*-aminophenylglyoxaline in the reduction of 2-benzeneazoglyoxaline, the yield of 2-amino-

glyoxaline is small, so for the preparation of this substance the reduction of an arylazoglyoxaline containing a substituent in the para-position of the benzene nucleus was undertaken.

2-p-*Bromobenzeneazoglyoxaline* is the main product of the inter-action of *p*-bromobenzenediazonium chloride and glyoxaline in aqueous sodium carbonate, only a very small proportion of 4-p-*bromobenzeneazoglyoxaline* being formed. The reduction of 2-*p*-bromobenzeneazoglyoxaline with stannous chloride gave 2-aminoglyoxaline in a yield of 56 per cent. of the theoretical, together with aniline, guanidine, some 2-amino-4-*p*-aminophenyl-glyoxaline, and a small quantity of a base, $C_9H_9N_4Br$, which is probably 2-5'-*bromo-2'-aminoanilinoglyoxaline* (compare p. 246).

2-Aminoglyoxaline is a monacidic base yielding crystalline salts, but the free base has not been obtained in a crystalline form.

$$\begin{matrix} \text{CH·NH} \\ | \quad \quad \\ \text{CH——N} \end{matrix} {>} \text{C·NH}_2 \qquad \qquad \begin{matrix} \text{CH·NH} \\ | \quad \quad \\ \text{CH·NH} \end{matrix} {>} \text{C:NH}$$

$$\text{(XII.)} \qquad \qquad \qquad \qquad \text{(XIII.)}$$
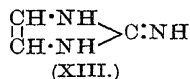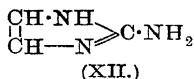
For this compound, the tautomeric formulæ (XII) and (XIII) are possible. The first is supported by the production of a red colour when the substance is mixed with sodium diazobenzene-*p*-sulphonate, and by the fact that, after treatment with nitrous acid, it couples with phenols. An indication that it can also react according to the formula (XIII)—which represents an unsaturated compound no longer containing the glyoxaline ring—is given by its behaviour towards permanganate, for 2-aminoglyoxaline and all the substituted 2-aminoglyoxalines described in this paper reduce cold aqueous acid potassium permanganate, and in this respect resemble the 2-thiolglyoxalines (compare T., 1911, **99**, 2173), whereas glyoxaline and its homologues are stable to this reagent, although they reduce alkaline permanganate, giving green solutions.

2-Aminoglyoxaline yields a *monoacetyl* and a *monobenzoyl* deriv-ative, which are stable to cold aqueous acid permanganate.

2-Aminoglyoxaline does not combine with benzaldehyde in acetic acid solution. Moreover, 2-amino-5-*p*-aminophenyl-4-methyl-glyoxaline (XVII) yields only a monobenzylidene compound under these conditions, doubtless 2-amino-5-*p*-benzylideneaminophenyl-4-methylglyoxaline. This behaviour, therefore, serves to differentiate between 2-aminoglyoxalines and homologues of aniline, and is employed later in the determination of constitution.

The action of benzenediazonium chloride on 4-methylglyoxaline proceeded quite differently from its action on glyoxaline. Instead of the 2-substituted arylazo-compound being formed predominantly,

nearly equal quantities of *2-benzeneazo-4-methylglyoxaline*, *5-benzeneazo-4-methylglyoxaline*, and *2 : 5-bisbenzeneazo-4-methylglyoxaline* were obtained. The constitution of 2-benzeneazo-4-methylglyoxaline (XIV) follows from the fact that it yields, on reduction with zinc dust and acetic acid, alacreatinine (XV), a compound previously synthesised by Baumann (*Annalen*, 1873, **167**, 83) by the elimination of water from α-guanidinopropionic acid (XVI).

$$\begin{array}{c} CMe{\cdot}NH \\ \| \\ CH{\cdot}\quad{\cdot}N \end{array}\!\!>\!\!C{\cdot}N{:}NPh \longrightarrow$$

(XIV.)

$$\begin{array}{c} CHMe{\cdot}NH \\ \| \\ CO{-}\!{-}{-}NH \end{array}\!\!>\!\!C{:}NH \longleftarrow \begin{array}{c} CHMe{\cdot}NH \\ \| \\ CO_2H\ NH \end{array}\!\!>\!\!C{:}NH$$
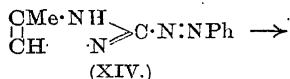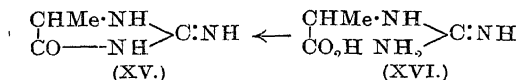
(XV.)　　　　　　　　　(XVI.)

This change is precisely similar to the formation of glycocyamidine from 2-benzeneazoglyoxaline. 2-Benzeneazo-4-methylglyoxaline behaves in the same way as 2-benzeneazoglyoxaline on reduction with stannous chloride, the principal product of the reaction being *2 - amino - 5 - p - aminophenyl - 4 - methylglyoxaline* (XVII), a compound having similar properties to 2-amino-4-*p*-aminophenylglyoxaline.

$$\begin{array}{c} NH_2{\cdot}C_6H_4{\cdot}C{-}\!{-}NH \\ \| \\ CMe{\cdot}N \end{array}\!\!>\!\!C{\cdot}NH_2 \qquad \begin{array}{c} PhN{:}N{\cdot}C{-}\!{-}NH \\ \| \\ CMe{\cdot}N \end{array}\!\!>\!\!CH$$
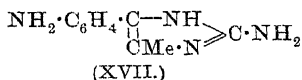
(XVII.)　　　　　　　　　　(XVIII.)
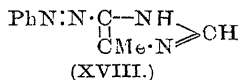
The constitution of 5-benzeneazo-4-methylglyoxaline (XVIII) could not be proved directly as in the case of the 2-isomeride. On reduction, aniline and a considerable amount of ammonia were formed, together with other products, which included a base, $C_9H_{10}ON_2$ (p. 254), when stannous chloride was employed as the reducing agent, and a base, $C_{10}H_{11}ON_8$ (p. 255), when zinc dust and acetic acid were used. The disintegration of the molecule indicated by the formation of ammonia is similar to that occurring in the reduction of the 4-nitroglyoxalines, and affords evidence that the constitution of the compound is represented correctly by the formula of 5-benzeneazo-4-methylglyoxaline. The formula is supported by the fact that the compound is soluble in dilute aqueous sodium hydroxide, which indicates that the imino-group is unsubstituted. Moreover, it is fairly stable towards boiling dilute acids. Its properties are not therefore in accord with those of a compound represented by the alternative formula, 1-benzeneazo-4-methylglyoxaline.

That aryldiazonium salts are capable of substituting the 4-position of the glyoxaline ring follows from the reduction of 2-*phenyl-*

4-p-*bromobenzeneazoglyoxaline*, $C_{15}H_{11}N_4Br$, for a *compound*, $C_{15}H_{13}N_4Br$, is produced, which is evidently derived from the corresponding hydrazo-compound by a change of the semidine or benzidine type (compare p. 257).

The polyarylazoglyoxalines—2 : 4 : 5-trisbenzeneazoglyoxaline and 2 : 5-bisbenzeneazo-4-methylglyoxaline—are insoluble in dilute mineral acids, and are decomposed on boiling with 10 per cent. hydrochloric acid. Nevertheless, we regard them as *C*-azo-compounds, because they are soluble to some extent in aqueous sodium hydroxide. In the case of the second compound, we have established the fact that it is precipitated unchanged from its solution in aqueous sodium hydroxide by means of acetic acid. The fact that the number of arylazo-groups in the polyarylazo-compounds corresponds with the number of nuclear methine groups in the parent glyoxaline points in the same direction.

The interaction of glyoxaline-4 : 5-dicarboxylic acid and diazobenzene-*p*-sulphonic acid was studied by Burian (*loc. cit.*), who found that carbon dioxide was liberated, and described a product forming yellow needles or red, microscopic prisms which gave on analysis results indicating that it was a compound derived from one molecular proportion of diazobenzene-*p*-sulphonic acid and one of glyoxaline - 4 - carboxylic acid, $SO_3H·C_6H_4·N:N·C_3H_2N_2·CO_2H$. Burian regarded this as a 1-substituted arylazoglyoxaline, but we thought it more probable that the arylazo-group had displaced a carboxyl group in the 4-(or 5-)position, and that the compound was 5-*p*-sulphobenzeneazoglyoxaline-4-carboxylic acid (XIX).

$$SO_3H·C_6H_4·N:N·C·NH$$
$$CO_2H·C——N\!\!>\!\!CH.$$
$$(\textbf{XIX.})$$
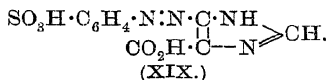
This compound would yield 5-aminoglyoxaline-4-carboxylic acid if a suitable method of reduction could be found, and we therefore attempted to repeat its preparation, but were unable to do so. We can confirm Burian's statement that carbon dioxide is liberated in the reaction, but find the yield of this to be only about 40 per cent. of the theoretical, much less than he states. Moreover, we have isolated in a yield of about 30 per cent. of the theoretical the condensation product of diazobenzene-*p*-sulphonic acid and glyoxaline-4 : 5-dicarboxylic acid, namely, 2-p-*sulphobenzeneazoglyoxaline*-4 : 5-*dicarboxylic acid* (XX). No other definite compound could be isolated from the reaction mixture, and it appears to us that the compound described by Burian was probably a mixture of our acid with its sodium salt.

2-*p*-Sulphobenzeneazoglyoxaline-4 : 5-dicarboxylic acid yields on

reduction with sodium hyposulphite, sulphanilic acid and 2-*amino-glyoxaline*-4 : 5-*dicarboxylic acid* (XXI).

$$\begin{matrix} CO_2H \cdot C \cdot NH \\ CO_2H \cdot C --- N \end{matrix} \!\!\!\!> C \cdot N \colon N \cdot C_6H_4 \cdot SO_3H \longrightarrow \begin{matrix} CO_2H \cdot C \cdot NH \\ CO_2H \cdot C --- N \end{matrix} \!\!\!\!> C \cdot NH_2$$

$$\qquad\qquad\text{(XX.)}\qquad\qquad\qquad\qquad\qquad\qquad\text{(XXI.)}$$
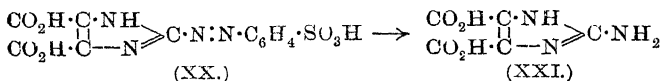
With the object of eliminating the elements of carbon dioxide, this acid was heated with water for twelve hours at 170°, when carbon dioxide and approximately one molecular proportion of ammonia were liberated, but no other fission product could be identified. On the other hand, when boiled with aniline for six hours, it gave a quantity of 2-aminoglyoxaline.

Whilst we were unable to isolate 5-*p*-sulphobenzeneazo-glyoxaline-4-carboxylic acid (XIX) from the products of the inter-action of diazobenzene-*p*-sulphonic acid and glyoxaline-4 : 5-dicarb-oxylic acid, the liberation of carbon dioxide indicates that sub-stitution in the 4-(or 5-)position takes place to some extent. More-over, we can confirm the fact that 2-methylglyoxaline-4 : 5-dicarb-oxylic acid couples with sodium diazobenzene-*p*-sulphonate in aqueous sodium carbonate.

On the other hand, 2 : 4 : 5-trimethylglyoxaline (XXII), which contains a free imino-group but no other hydrogen atom attached

$$\begin{matrix} CMe \cdot NH \\ CMe --- N \end{matrix} \!\!\!\!> CMe$$

$$\text{(XXII.)}$$
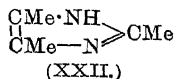
to the nucleus, does not couple with sodium diazobenzene-*p*-sulphonate. Further, a striking difference is exhibited between the facilities with which 2-amino-4-*p*-aminophenylglyoxaline (VI) containing a displaceable hydrogen atom in the glyoxaline nucleus and its methyl homologue (XVII) react with sodium diazobenzene-*p*-sulphonate in aqueous sodium carbonate. The first gives the characteristic intense cherry-red colour immediately, whilst the second gives a pale orange colour which deepens on keeping, and is probably due to the participation of the aminophenyl group.

On reviewing these results and those of previous investigators, it appears to us that glyoxalines, in order to be capable of coupling, must contain a free imino-group and also a hydrogen atom, or some other displaceable group, such as the carboxyl group, in one of the 2-, 4-, or 5-positions, and that the arylazoglyoxalines hitherto pre-pared are *C*-azo-compounds.

The literature of the arylazoglyoxalines contains one possible exception to this generalisation—the compound (orange needles melting at 120—122°) described by Burian (*loc. cit.*) as having been obtained by the action of diazotised benzidine on 2-thiol-4 : 5-

diphenylglyoxaline. Since we found that 2-thiol-4:5-dimethyl-glyoxaline and 2-thiol-4:5-diphenylglyoxaline only gave pale orange colorations with sodium diazobenzene-p-sulphonate, we repeated Burian's preparation. We failed, however, to confirm his results, but isolated from the product, as main constituents, much unchanged 2-thiol-4:5-diphenylglyoxaline and a reddish-brown, amorphous compound, melting and decomposing above 200°, which from its low nitrogen content (5·5 per cent.) and the ratio of nitrogen to sulphur (2:1) could not have been an arylazo-derivative derived from 2-thiol-4:5-diphenylglyoxaline.

Experimental.

Part I. *Glyoxalines and their Carboxylic Acids.*

Preparation of Glyoxaline-4:5-dicarboxylic Acid.

Twenty-five grams of finely powdered tartaric acid are dissolved in 108 c.c. of nitric acid (D 1·5), and 125 c.c. of sulphuric acid are added. The mixture, which attains a temperature of about 40°, soon begins to deposit crystals, and is kept for three to four hours in a cool place. The nitrotartaric acid is collected, washed with 50 per cent. sulphuric acid, drained on porous porcelain, and stirred immediately with 150 grams of powdered ice until dissolved, when the temperature falls to $-5°$.

The liquid is immersed in a freezing mixture, and 100 c.c. of aqueous ammonia (D 0·880) are added gradually, the temperature being kept below 0°. Then 50 c.c. of 40 per cent. aqueous formaldehyde are added slowly, keeping the temperature below 10°. The product is removed from the freezing mixture after three to four hours, and kept overnight. It is then mixed with a little alcohol and acidified with hydrochloric acid, when 15·5 to 16·0 grams of glyoxaline-4:5-dicarboxylic acid separate, that is, about 60 per cent. of the theoretical yield calculated on the quantity of tartaric acid employed.

Glyoxaline-4:5-dicarboxylic acid melts and effervesces at 288° (corr.). It is soluble in about 800 parts of boiling water and in about 2000 parts of cold water. It is practically insoluble in the usual organic solvents, but dissolves sparingly in pyridine. It is soluble in concentrated mineral acids, but is precipitated unchanged on dilution with water. The *monosodium* salt, which crystallises from water as a felted mass of feathery needles containing $1H_2O$ (Found: $H_2O = 9·4$; in dried salt, $Na = 12·8$. Calc.: $H_2O = 9·2$; $Na = 12·9$ per cent.), is sparingly soluble in water but readily so in aqueous sodium hydr-

oxide, probably owing to the formation of a disodium salt in solution. Moreover, the addition of alcohol to a solution of the acid in sufficient aqueous sodium hydroxide to form the disodium salt causes the precipitation of a granular deposit approximating in composition to the disodium salt. (Found, in salt dried at 110°, $Na = 21.2$. $C_5H_2O_4N_2Na_2$ requires $Na = 23.0$ per cent.)

The acid is very stable towards nitric acid; after boiling it with ten times its weight of concentrated nitric acid for twenty-four hours, more than 90 per cent. was recovered unchanged, whilst similar results were obtained in a sealed tube at 130°, and when the acid was boiled with equal parts of nitric and sulphuric acids.

The acid is very resistant to esterification, for, after boiling with alcoholic sulphuric acid for twenty-four hours, 95 per cent. was recovered unchanged.

The Preparation of Glyoxaline.

One hundred grams of glyoxaline-4:5-dicarboxylic acid were distilled, under normal pressure, in quantities of 4 grams from a small flask into a long, wide air condenser. The distillate, which had solidified in the condenser, was crystallised from benzene, and gave a 92 per cent. yield of the pure base.

Glyoxaline picrate crystallises from water in long, fine, yellow needles, which become orange on drying at 100°, and then melt at 212° (corr.), after sintering from 208°. It contains rather more than $1H_2O$ (Found, loss at $100° = 7.2$; in substance dried at 100°, $N = 23.3$. $C_3H_4N_2,C_6H_3O_7N_3$ [297.1] requires $N = 23.6$ per cent.).

Glyoxaline hydrogen tartrate crystallises from water in fine prisms of characteristic trapezoidal shape, which are anhydrous and melt at 202° (corr.). It is readily soluble in cold water, and is best crystallised from 50 per cent. alcohol (Found: $N = 12.8$. $C_3H_4N_2,C_4H_6O_6$ [218.1] requires $N = 12.8$ per cent.).

Glyoxaline hydrogen oxalate crystallises from water as a felted mass of prismatic needles, which are anhydrous and melt at 232° (corr.) after sintering from 230°. It is soluble in five or six parts of boiling water, but much less so in cold water (Found: $N = 17.8$. Calc.: $N = 17.7$ per cent.).

Action of Boiling Aniline on Glyoxaline-4:5-dicarboxylic Acid: Formation of Glyoxaline-4-carboxyanilide and Glyoxaline.

Five grams of glyoxaline-4:5-dicarboxylic acid were boiled with 50 c.c. of aniline for nine hours under a reflux condenser, when

the acid gradually passed into solution. The product was mixed with water and subjected to distillation with steam until the excess of aniline had been removed. The residual aqueous solution was filtered from a small quantity of resinous matter whilst still hot, when the filtrate at once began to deposit the anilide as a felted mass of fine needles. The first crop amounted to 2·6 grams, and a further quantity of 0·1 gram was obtained on concentrating the mother liquor. The filtrate from this gave on acidification 0·1 gram of glyoxaline-4:5-dicarboxylic acid, but no glyoxaline-4-carboxylic acid was found. The final mother liquor when mixed with sodium carbonate, evaporated to dryness, and extracted with benzene gave 0·9 gram of glyoxaline.

Glyoxaline-4-carboxyanilide crystallises from boiling water in fine, colourless needles, which are anhydrous and melt at 227—228° (corr.). It is fairly readily soluble in alcohol, but only sparingly so in boiling water and the other usual organic solvents.

Found: $C = 64·2$; $H = 5·1$; $N = 22·6$.
$C_{10}H_9ON_3$ (187·15) requires $C = 64·2$; $H = 4·9$; $N = 22·5$ per cent.

Hydrolysis of the Anilide.—The anilide is only slowly hydrolysed by 10 per cent. hydrochloric acid at 100°, but more readily at 130°.

One gram of the anilide was heated with 10 c.c. of 10 per cent. hydrochloric acid at 130° for three hours. The resulting solution was evaporated to dryness to remove the excess of acid, the residue dissolved in water, basified with sodium carbonate, and extracted with ether to remove aniline. Sufficient hydrochloric acid was added to render the solution faintly acid to methyl-orange, when crystallisation set in almost immediately, and 0·42 gram of glyoxaline-4-carboxylic acid was isolated The properties of the acid and its hydrochloride, nitrate, and picrate agreed with those previously given (T., 1916, **109**, 199) for the acid prepared by the oxidation of 4-hydroxymethylglyoxaline, and the melting points of mixtures of the compounds from the two sources were not depressed.

2-*Methylglyoxaline*-4:5-*dicarboxylic Acid.*

This acid was prepared in an analogous manner to its lower homologue, employing a solution of 15 c.c. of freshly distilled acetaldehyde dissolved in 50 c.c. of ice-water in the place of the aqueous formaldehyde. The yield of 2-methylglyoxaline-4:5-dicarboxylic acid, containing $1H_2O$, obtained from 25 grams of tartaric acid was 22 grams, that is, 67 per cent. of the theoretical.

Maquenne (*loc. cit.*) obtained 50 grams of the product from 100 grams of tartaric acid, that is, 38 per cent. of the theoretical.

Generally, the properties of this acid are very similar to those of glyoxaline-4 : 5-dicarboxylic acid, and it behaves similarly on acid and alkaline hydrolysis.

With sodium diazobenzene-*p*-sulphonate in aqueous sodium carbonate, it gives a faint red colour which deepens on keeping, whilst glyoxaline-4 : 5-dicarboxylic acid gives a deeper red colour in the first instance.

Action of Boiling Aniline on 2-Methylglyoxaline-4 : 5-dicarboxylic Acid.

Twenty grams of hydrated 2-methylglyoxaline-4 : 5-dicarboxylic acid, when treated with boiling aniline under the same conditions as its lower homologue, gave 11 grams of the hydrated anilide of 2-methylglyoxaline-4-carboxylic acid and 3·8 grams of 2-methyl-glyoxaline.

2-Methylglyoxaline-4-carboxyanilide crystallises from boiling water as a felted mass of colourless, silky needles, which contain rather less than $1H_2O$. It is sparingly soluble in boiling water, but readily so in alcohol. After drying at 110°, it melts at 208° (corr.).

Found, loss at 110° in three samples = 6·9, 7·0, 7·2.

$C_{11}H_{11}ON_3,H_2O$ requires $H_2O = 8·2$ per cent.

Found, in substance dried at 110°, C = 65·1, 65·6; H = 5·7, 5·6; N = 20·9.

$C_{11}H_{11}ON_3$ (201·2) requires C = 65·6; H = 5·5; N = 20·9 per cent.

2-Methylglyoxaline-4-carboxylic acid is obtained in nearly the theoretical yield by the hydrolysis of its anilide under similar conditions to those already described for glyoxaline-4-carboxylic acid. When placed in a bath at 250°, it melts and effervesces at 262° (corr.). It crystallises from water in clusters of prismatic needles containing $1H_2O$. It is soluble in about twenty parts of boiling water, but is practically insoluble in the usual organic solvents.

Found, loss at 110° = 12·9.

$C_5H_6O_2N_2,H_2O$ requires $H_2O = 12·5$ per cent.

Found, in the substance dried at 110°, C = 47·3; H = 4·8; N = 21·9.

$C_5H_6O_2N_2$ (126·1) requires C = 47·6; H = 4·8; N = 22·2 per cent.

With sodium diazobenzene-*p*-sulphonate it gives a red colour in sodium carbonate solution.

The *hydrochloride* crystallises from water, in which it is readily

soluble, in minute, flattened, rhombic prisms, which are anhydrous. It melts and effervesces at 268° (corr.).

Found: $N = 16.9$; $Cl = 21.5$.

$C_5H_6O_2N_2,HCl$ (162·6) requires $N = 17.2$; $Cl = 21.8$ per cent.

The *nitrate* crystallises from water, in which it is very readily soluble, in minute rhombic prisms, which melt and effervesce at 190° (corr.), resolidify, and on further heating gradually darken, melting at about 240°.

Found: $C = 31.7$; $H = 4.1$.

$C_5H_6O_2N_2,HNO_3$ (189·1) requires $C = 31.7$; $H = 3.7$ per cent.

The *picrate* crystallises from water in minute cubes containing $2H_2O$, which is lost at 100° (Found: $H_2O = 9.4$. Calc. for $2H_2O$, 9·2 per cent.). It melts to a turbid liquid at 200° (corr.), which does not become clear until 224°, at which temperature effervescence begins.

Found, in salt dried at 100°, $N = 19.4$.

$C_5H_6O_2N_2,C_6H_3O_7N_3$ (355·2) requires $N = 19.7$ per cent.

2-Methylglyoxaline picrate crystallises from boiling water in fine needles, which are anhydrous and melt at 213° (corr.).

Found: $N = 22.3$.

$C_4H_6N_2,C_6H_3O_7N_3$ (311·2) requires $N = 22.5$ per cent.

2-Methylglyoxaline hydrogen oxalate crystallises from water in large, rhombic prisms which contain $2H_2O$ (Found: $H_2O = 17.6$. Calc. for $2H_2O$: $H_2O = 17.3$ per cent.). After drying at 100°, it melts at 160° (corr.), and effervesces on further heating. It is much more readily soluble in water than the corresponding glyoxaline salt.

Found, in dried salt: $N = 16.1$.

$C_4H_6N_2,C_2H_2O_4$ (172·1) requires $N = 16.3$ per cent.

2-*Ethylglyoxaline*-4 : 5-*dicarboxylic Acid.*

This acid was prepared in the same way as the methyl substituted acid. From 32 c.c. of propaldehyde, and the nitrotartaric acid obtained from 50 grams of tartaric acid, 43 grams of hydrated 2-ethylglyoxaline-4 : 5-dicarboxylic acid were obtained, that is, 64 per cent. of the theoretical yield; Maquenne obtained 30 per cent. 2-Ethylglyoxaline-4 : 5-dicarboxylic acid melts and effervesces at 259° (corr.).

2-*Phenylglyoxaline*-4 : 5-*dicarboxylic Acid*.

The nitrotartaric acid from 25 grams of tartaric acid was treated with 100 c.c. of aqueous ammonia in the manner previously described. Then 20 grams of benzaldehyde were added, with stirring, below 0°, and the stirring was continued for seven hours, the temperature of the mixture being gradually allowed to approach that of the room. After keeping overnight, 17·1 grams of 2-phenylglyoxaline-4 : 5-dicarboxylic acid were isolated, that is, 48 per cent. of the theoretical yield, whereas Maquenne's yield was only 8 per cent. 2-Phenylglyoxaline-4 : 5-dicarboxylic acid melts and effervesces at 271° (corr.).

When distilled under the conditions previously described in the case of glyoxaline-4 : 5-dicarboxylic acid, it gives 2-phenylglyoxaline in a yield of more than 80 per cent. of the theoretical.

2-Phenylglyoxaline crystallises from water in small, prismatic needles, which melt at 148—149° (corr.) and are anhydrous.

2-*Phenylglyoxaline nitrate* is readily soluble in water, but less so in alcohol, from which it separates in leaflets containing $\frac{3}{4}H_2O$, which is lost at 60° in a vacuum. The dried salt melts at 135° (corr.).

Found, in air-dried salt, $H_2O = 6·1$; in dried salt, $N = 20·0$.

$C_9H_8N_2,HNO_3$ (207·1) requires $N = 20·3$ per cent.

The *hydrogen oxalate* crystallises from water in flattened needles, which melt and effervesce at 219° (corr.), and are anhydrous. It is readily soluble in hot water, but less so in cold.

Found: $N = 12·0$.

$C_9H_8N_2,C_2H_2O_4$ (234·1) requires $N = 12·0$ per cent.

The *picrate* is sparingly soluble even in boiling water, from which it crystallises in fine needles which melt at 238° (corr.), and are anhydrous.

Found: $N = 18·6$.

$C_9H_8N_2,C_6H_3O_7N_3$ (373·2) requires $N = 18·8$ per cent.

4 : 5-*Dimethyl*- and 2 : 4 : 5-*Trimethyl-glyoxaline*.

When 4 : 5-dimethylglyoxaline is prepared by Windaus' method (*Ber.*, 1909, **42**, 758), it is contaminated with 2 : 4 : 5-trimethylglyoxaline, which results from the interaction of diacetyl and ammonia (von Pechmann, *Ber.*, 1888, **21**, 1414).

8·6 Grams of diacetyl were dissolved in 50 c.c. of water, 50 c.c. of 40 per cent. aqueous formaldehyde added, the mixture cooled to 0°, and 80 c.c. of concentrated ammonia solution gradually

added, the reaction mixture being stirred and kept below 0°. After the addition was ended, the mixture was allowed to remain in a cool place overnight, then evaporated to a low bulk, saturated with anhydrous potassium carbonate, and the oil which separated extracted by ether. The crude extract, which was contaminated with hexamine, amounted to 5·9 grams. After destruction of the hexamethylenetetramine by boiling dilute hydrochloric acid, the picrates of the constituent bases were fractionated from water, when 5·7 grams of 4:5-dimethylglyoxaline picrate (17·5 per cent. of the theoretical yield) were obtained first, and then 3·5 grams of 2:4:5-trimethylglyoxaline picrate.

2:4:5-*Trimethylglyoxaline picrate* sinters from 160° and melts at 163° (corr.). It crystallises from water in well-defined prisms, which are often serrated.

Found : N = 20·6.
$$C_6H_{10}N_2, C_6H_3O_7N_3 \text{ requires } N = 20\cdot6 \text{ per cent.}$$

The hydrochloride, previously prepared by von Pechmann, crystallises from alcohol in fine needles, which are anhydrous and melt at 316° (corr.) (Found : N = 19·0; Cl = 24·2. Calc.: N = 19·1; Cl = 24·2 per cent.).

4:5-*Dimethylglyoxaline hydrochloride* crystallises from alcohol in well-defined, rhombic prisms which melt and decompose at 305° (corr).

Found : N = 21·1; Cl = 26·4.
$$C_5H_8N_2, HCl \text{ requires } N = 21\cdot1 ; Cl = 26\cdot7 \text{ per cent.}$$

4:5-Dimethylglyoxaline was also prepared by a modification of Künne's method (*Ber.*, 1895, **28**, 2039; compare also Jowett, T., 1905, **87**, 407). Nine grams of methyl α-*iso*nitrosoethyl ketone were reduced with stannous chloride, as described by Künne, but the temperature of the reaction mixture was maintained at 15°, and, after the removal of the tin, the evaporation of the liquor was conducted entirely under diminished pressure. By these means, a yield of 10 grams of crude, crystalline methyl α-aminoethyl ketone hydrochloride was obtained, as against 4·2 grams of syrup obtained by Künne. When this product was heated on the water-bath for four hours with 10 grams of potassium thiocyanate and 40 c.c. of water, 5·2 grams of 2-thiol-4:5-dimethylglyoxaline separated, and this gave 4:5-dimethylglyoxaline picrate in a yield of 85 per cent. of the theoretical when oxidised with the calculated quantity of ferric chloride.* The yield of 4:5-dimethylglyoxaline from methyl ethyl ketone is thus 23·8 per cent. of the theoretical.

* The method of oxidising thiolglyoxalines to glyoxalines by means of ferric chloride has been described by one of us (T., 1911, **99**, 2175) in the case of

Part II. Nitroglyoxalines.

4-Nitroglyoxaline.

Rung and Behrend (*loc. cit.*) prepared 4-nitroglyoxaline in a yield of 36 per cent. of the theoretical by boiling glyoxaline with a mixture of nitric and sulphuric acids. The yield can be improved greatly by the method given below. Eight grams of glyoxaline were dissolved in 16 c.c. of nitric acid (D 1·4), cooled, and 16 c.c. of sulphuric acid cautiously added. A vigorous reaction ensued, and when this had subsided the mixture was boiled gently for two hours, allowed to cool, and then poured into ice-water, when 7·85 grams of 4-nitroglyoxaline separated. The mother liquors yielded a further 0·5 gram of 4-nitroglyoxaline identical with the above, but no glyoxaline and merely a trace of other crystalline material. The total yield of 4-nitroglyoxaline thus amounted to 63 per cent. of the theoretical. 4-Nitroglyoxaline crystallises from boiling acetic acid or from alcohol in stout, rhombic prisms, which are anhydrous and melt at 312—313° (corr.) (Found: $N = 36·8$. Calc.: $N = 37·1$ per cent.). It is only very sparingly soluble in boiling water. Although it dissolves in strong mineral acids, it is precipitated unchanged on the addition of water, and is recovered unchanged when crystallised from aqueous picric acid.

4-Nitro-2-methylglyoxaline was similarly prepared. It crystallises from water in fine needles, which are anhydrous and melt at 254° (corr.), sintering from 251°.

Found: $N = 33·0$.

$C_4H_5O_2N_3$ (127·1) requires $N = 33·1$ per cent.

5-Nitro-4-methylglyoxaline was prepared by Windaus (*loc. cit.*) in a 60 per cent. yield by warming 4-methylglyoxaline with fuming nitric acid at 80°. Using this method, we found the main product to be 4-methylglyoxaline nitrate. Proceeding according to the method described for 4-nitro-2-methylglyoxaline, 5 grams of 4-methylglyoxaline gave 7 grams of 5-nitro-4-methylglyoxaline (Found: $N = 32·8$. Calc.: $N = 33·1$ per cent.) melting at 248° (corr.), that is, 90 per cent. of the theoretical yield.

2-thiol-4-aminomethylglyoxaline. The low yield of 4-aminomethylglyoxaline recorded (56 per cent. of the theoretical) was due to the fact that insufficient ferric chloride had been employed. When the calculated quantity (16·2 grams) of this reagent is used, the product is obtained in a yield of 90 per cent. of the theoretical.

Attempted Nitration of 4:5-*Dimethylglyoxaline.*

To five grams of 4:5-dimethylglyoxaline dissolved in 15 c.c. of nitric acid (D 1·4), 15 c.c. of sulphuric acid were added. The first vigorous reaction was controlled by cooling, and after it had ended the mixture was heated for two hours on the water-bath. From the reaction product, 1·7 grams of 4:5-dimethylglyoxaline were recovered, together with 0·3 gram of the nitrate of 4-methyl-glyoxaline-5-carboxylic acid (Found: $C = 32·1$; $H = 4·0$; $N = 21·7$. Calc.: $C = 31·6$; $H = 3·7$; $N = 22·1$ per cent.), which deposited the corresponding acid, melting and effervescing at 222°, on the addition of the calculated quantity of sodium hydroxide. From the pure acid, the hydrochloride, which melted and decomposed at 231°, and the nitrate, which decomposed at 189°, were prepared. The melting points of the acid and its salts are in agreement with those found by Gerngross (*loc. cit.*) for 4-methylglyoxaline-5-carboxylic acid.

Reduction of Nitroglyoxalines with Tin and Hydrochloric Acid.

When 4-nitroglyoxaline, 4-nitro-2-methylglyoxaline, or 5-nitro-4-methylglyoxaline is reduced with tin and hydrochloric acid, and the product mixed with sodium hydroxide and distilled into standard acid, two of the three atoms of nitrogen present in the molecule are eliminated in the form of ammonia:

    0·5609 of 4-nitroglyoxaline gave 0·1746 NH_3; calc. as above, 0·1688.

    0·4292 of 4-nitro-2-methylglyoxaline gave 0·118 NH_3; calc. as above, 0·115.

    0·4931 of 5-nitro-4-methylglyoxaline gave 0·1378 NH_3; calc. as above, 0·1320.

That the greater part of the ammonia is actually produced during the reduction, and not by the subsequent action of the alkali, is shown in the case of 4-nitroglyoxaline by the following experiment.

Twelve grams of 4-nitroglyoxaline were reduced by means of tin and hydrochloric acid in the usual manner. The reduced liquors were freed from tin and then evaporated to dryness, then moistened with alcohol, and again evaporated to remove water as far as possible. The crude product was extracted with alcohol and left 9 grams of a crystalline solid, which proved to be ammonium chloride (Found: $N = 25·9$; $Cl = 66·0$. Calc.: $N = 26·2$;

Cl = 66·3 per cent.). The residue of the purple alcoholic solution gave 5 grams of an insoluble phosphotungstate after the removal of ammonia. This product has not yet been investigated.

Reduction of Nitroglyoxalines with Sodium Hyposulphite.

Behrend and Schmitz (*loc. cit.*) observed that 4-nitroglyoxaline gave a beautiful blue dye when treated with alkaline reducing agents. We can confirm this result, but find that ammonia is also produced in an amount corresponding with the loss of two atoms of nitrogen in this form from three molecules of 4-nitroglyoxaline when this compound is reduced with sodium hyposulphite in aqueous sodium hydroxide:

0·5148 of 4-nitroglyoxaline gave 0·0521 NH_3; calc. as above, 0·0516.

The liquors remaining from the distillation gradually acquired a dark blue colour on exposure to the air, and on acidification with acetic acid deposited rather less than 0·1 gram of a blue compound which did not melt below 300°.

The reduction of 5-nitro-4-methylglyoxaline with alkaline sodium hyposulphite led to the same result as in the case of 4-nitroglyoxaline, two molecules of ammonia being produced from three molecules of the nitro-compound (0·5311 gave 0·0487 NH_3; calc. as above, 0·0474). The reduced solution gradually acquired a rose colour on exposure to air, but gave no precipitate with acetic acid.

4-Nitro-2-methylglyoxaline behaved differently from the above compounds on reduction with alkaline sodium hyposulphite, yielding one molecule of ammonia from three molecules of the nitro-compound (0·5084 gave 0·0230 NH_3; calc. as above, 0·0227).

Part III.   Arylazoglyoxalines.
2-Benzeneazoglyoxaline (IV, p. 221).

23·25 Grams of aniline were dissolved in 62·5 c.c. of hydrochloric acid and 187·5 c.c. of water, and diazotised with 18 grams of sodium nitrite dissolved in 100 c.c. of water. The solution was run slowly into a well-stirred solution of 17 grams of glyoxaline and 40 grams of anhydrous sodium carbonate in 1250 c.c. of water, previously cooled to 5°, and kept overnight. The insoluble orange powder was collected, washed well with water, and extracted successively with 250, 125, and 125 c.c. of cold 2·5 per cent. hydrochloric acid. (Extract = *A*.) The insoluble material amounted to 4·4

grams, and after crystallisation from alcohol gave 2:4:5-*trisbenzeneazoglyoxaline*, of which only 0·5 gram was obtained in a pure state. This compound decomposes at about 200° and effervesces at 208° (corr.). When pure, it is only sparingly soluble even in boiling alcohol, from which it crystallises slowly in dark brown clusters of crystals of indeterminate shape. (0·84 required 60 c.c. of boiling alcohol.)

Found: C = 66·0; H = 4·6; N = 29·0.

$C_{21}H_{16}N_8$ (380·3) requires C = 66·3; H = 4·2; N = 29·5 per cent.

Trisbenzeneazoglyoxaline is insoluble in cold dilute hydrochloric acid, and is decomposed when boiled with this reagent. It dissolves to some extent in aqueous sodium hydroxide.

The hydrochloric acid extract (*A*) was diluted with water and basified with sodium carbonate, when crude 2-benzeneazoglyoxaline was obtained as a yellow, crystalline precipitate, which, after thorough washing with cold water and drying, amounted to 34 grams. On crystallisation from 150 c.c. of alcohol, 31 grams of the pure base were obtained, that is, 74 per cent. of the theoretical. No other definite compound could be isolated from the mother liquor.

2-*Benzeneazoglyoxaline* crystallises from alcohol in large, orange tablets resembling potassium dichromate in appearance. It melts at 190° (corr.) to a reddish-black liquid.

Found: C = 62·7, 62·7; H = 4·8, 4·9; N = 32·3

$C_9H_8N_4$ (172·1) requires C = 62·8; H = 4·7; N = 32·6 per cent.

Rung and Behrend's Method.—By this method, in which benzene-diazonium chloride is allowed to react with glyoxaline without the addition of alkali, 5 grams of glyoxaline gave 3·3 grams of crude precipitate insoluble in water. Of this, 2·2 grams were separated into 0·7 gram of insoluble resin, which appeared to evolve gas on keeping, and 1·45 grams soluble in acid, which gave pure 2-benzeneazoglyoxaline on crystallisation from alcohol. The crude precipitate was less readily purified by direct crystallisation from alcohol.

General Properties of Arylazoglyoxalines.—To avoid repetition, it will be convenient to describe the general properties of the monoarylazoglyoxalines at this point. 2-Benzeneazoglyoxaline and 2-benzeneazo-4-methylglyoxaline are fairly readily soluble in alcohol, ethyl acetate, or acetone, sparingly so in ether, chloroform, or benzene. 5-Benzeneazo-4-methylglyoxaline, 2-*p*-bromobenzeneazoglyoxaline, and 4-*p*-bromobenzeneazo-2-methylglyoxaline are sparingly soluble in the first three solvents and very sparingly so in the last three.

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These compounds are almost insoluble in cold water or in dilute aqueous ammonia or sodium carbonate, but dissolve to some extent in dilute aqueous sodium hydroxide. The benzeneazo-compounds dissolve readily in dilute hydrochloric acid, and the solutions yield crystalline hydrochlorides on concentration ; the hydrochlorides of the *p*-bromobenzeneazo-compounds are sparingly soluble in water.

The stability of a 2- and a 4-substituted member of the group towards boiling dilute hydrochloric acid was examined. When 0·5 gram of 2-benzeneazoglyoxaline was boiled with 20 c.c. of 10 per cent. aqueous hydrochloric acid for two hours under a reflux condenser, 0·35 gram was recovered little changed on the addition of ammonia, and readily gave the starting material in a pure state on crystallisation from alcohol.

When 5-benzeneazo-4-methylglyoxaline was boiled with an excess of 10 per cent. aqueous hydrochloric acid for a few minutes, it was recovered unchanged after the addition of ammonia, but after boiling for one hour it was mainly decomposed, with the form-ation of resinous compounds.

The arylazoglyoxalines dissolve in concentrated sulphuric acid, giving bright-coloured solutions. The monoarylazo-derivatives yield mainly orange or magenta solutions, the 2-substituted deriv-atives being more intensely coloured than the 4-substituted com-pounds, whilst the solutions of bis- and tris-arylazoglyoxalines are green and still more intense than those of the 2-monoarylazo-derivatives.

Reduction of 2-Benzeneazoglyoxaline with Stannous Chloride: Isolation of 2-Amino-4-p-aminophenylglyoxaline, 2-Amino-glyoxaline, Guanidine, and Aniline.

Twenty grams of 2-benzeneazoglyoxaline were dissolved in 200 c.c. of boiling 2·5 per cent. hydrochloric acid and mixed with 120 c.c. of stannous chloride solution.* The solution was immedi-ately decolorised, and when mixed with 200 c.c. of hydrochloric acid deposited a crystalline tin salt (*A*). This was collected, and the mother liquor was evaporated to dryness, dissolved in hot water, and freed from tin. It was then evaporated to low bulk, mixed with sodium carbonate, and extracted with ether, which removed 3·0 grams of crude aniline. The alkaline liquor was acidified faintly with hydrochloric acid, evaporated to dryness, and extracted with alcohol, when 3·1 grams of extract were obtained. This was

* The stannous chloride solution employed throughout this investigation was made by mixing 40 grams of " tin salt " with sufficient hydrochloric acid to make 100 c.c. of solution.

mixed with stannic chloride, and deposited, first, 2·2 grams of pure
2-*aminoglyoxaline stannichloride*, then crops of the crude salt, from
which a further quantity of 1·0 gram of the pure salt was obtained,
the total yield amounting to 11 per cent. of the theoretical. The
final stannichloride mother liquors were deprived of tin by means
of hydrogen sulphide and mixed with picric acid. After crystal-
lisation from water, the first crop of picrate, which melted at 325°,
was decomposed by sulphuric acid, the picric acid being removed
by means of ether. The solution of sulphates was deprived of
sulphuric acid by barium hydroxide, and from excess of this
reagent by carbon dioxide. The resulting solution was neutralised
with aqueous oxalic acid, mixed with as much more aqueous oxalic
acid, and concentrated, when crude guanidine hydrogen oxalate
separated. After recrystallisation from water, this amounted to
0·07 gram, melting and effervescing at 172—173° (corr.) alone or
when mixed with pure guanidine hydrogen oxalate.

The crystalline tin salt (*A*) was dissolved in water, treated with
hydrogen sulphide, filtered from tin sulphide, and concentrated,
when 18·55 grams of 2-*amino*-4-p-*aminophenylglyoxaline dihydro-
chloride* separated, that is, 64·6 per cent. of the theoretical yield.

2-*Amino*-4-p-*aminophenylglyoxaline*, $C_9H_{10}N_4$ (VI, p. 222).

When the dihydrochloride is mixed with an equivalent quantity
of sodium carbonate, a colourless oil separates which solidifies on
keeping. This is a carbonate, for it effervesces on treatment with
acid, and when dissolved in boiling water disengages carbon dioxide
vigorously on the addition of animal charcoal, leaving a solution
of the free base, which crystallises on keeping. This solution
becomes brown at the top owing to oxidation in the air, whilst the
laminæ become mauve where exposed to the light.

To 5·0 grams of the dihydrochloride in 50 c.c. of boiling water,
30 c.c. of hot 10 per cent. aqueous sodium carbonate and a pinch
of animal charcoal were added. The solution was boiled for five
minutes, filtered, and kept, when 3·1 grams of the base separated
and were recrystallised from water. This base crystallises from
water in glistening leaflets which melt and effervesce at 148° (corr.).
It contains $1H_2O$, which is not lost in a vacuum or on heating at
100°.

Found: C=56·3; H=6·4; N=29·5, 29·2.
$C_9H_{10}N_4, H_2O$ (192·2) requires C=56·2; H=6·3; N=29·2 per cent.

It is sparingly soluble in cold, fairly readily so in hot water;
fairly readily soluble in cold, readily in hot alcohol, and very
sparingly so in chloroform or ether.

An aqueous solution of the base gives, with silver nitrate, a white precipitate, which blackens at once on the addition of ammonia; with Fehling's solution, a nearly black precipitate—presumably a copper salt—which is unchanged on boiling the solution; with cold permanganate, instant reduction; with sodium diazobenzene-p-sulphonate in aqueous sodium carbonate, an immediate cherry-red colour. When the base is dissolved in an excess of hydrochloric acid and mixed with sodium nitrite, a yellow solution is obtained, which yields with a solution of β-naphthol in aqueous sodium hydroxide a sparingly soluble purple dye. On the addition of sodium hydroxide to a solution containing 2-amino-4-p-aminophenylglyoxaline hydrochloride and sodium nitroprusside, a green coloration changing to chestnut-brown is produced.

On the addition of dilute sulphuric acid to an aqueous solution of the base or its hydrochloride, the very sparingly soluble sulphate crystallises in woolly needles.

The *dihydrochloride* crystallises from dilute hydrochloric acid in colourless prisms, which do not melt below 300°. It is readily soluble in cold, very readily so in hot water.

Found: Cl = 28·6; N = 22·5.

$C_9H_{10}N_4,2HCl$ (247·1) requires Cl = 28·7; N = 22·7 per cent.

The *dipicrate* forms yellow, silky needles, which darken at 245° and decompose at 250° (corr.). It is very sparingly soluble even in boiling water.

The benzylidene derivative of 2-amino-4-p-aminophenylglyoxaline was not obtained in a crystalline form.

2-*Acetylamino*-4-p-*acetylaminophenylglyoxaline.*

10·6 Grams of 2-amino-4-p-aminophenylglyoxaline were boiled with 50 c.c. of acetic anhydride for one hour under a reflux condenser and mixed with aqueous sodium carbonate, when 13·9 grams of the diacetyl derivative were obtained, that is, 98 per cent. of the theoretical yield. The base forms a colourless, crystalline powder which does not melt below 300°.

Found: N = 21·2.

$C_{13}H_{14}O_2N_4$ (258·2) requires N = 21·7 per cent.

It dissolves in dilute hydrochloric acid, but the hydrochloride crystallises almost at once. It appears to be changed by prolonged boiling with hydrochloric acid.

The *hydrochloride* was consequently prepared by triturating the base with an excess of 10 per cent. aqueous hydrochloric acid, draining the insoluble salt, and crystallising it from water, when it

formed colourless, prismatic needles, which did not melt below 300°. It is sparingly soluble in cold, fairly readily so in hot water.

Found, in air-dried salt, loss at $110° = 11\cdot1$.

$C_{13}H_{14}O_2N_4,HCl,2H_2O$ (330·7) requires $2H_2O = 10\cdot9$ per cent.

Found, in salt dried at 110°, $C = 53\cdot1$; $H = 5\cdot3$; $N = 18\cdot7$; $Cl = 11\cdot6$.

$C_{13}H_{14}O_2N_4,HCl$ (294·7) requires $C = 53\cdot0$; $H = 5\cdot1$; $N = 19\cdot0$; $Cl = 12\cdot0$ per cent.

Oxidation.—Ten grams of 2-acetylamino-4-*p*-acetylaminophenyl-glyoxaline were suspended in 150 c.c. of cold water and mixed with 4 grams of 50 per cent. aqueous sulphuric acid, when a suspension of the sulphate resulted. To this, cold 4 per cent. aqueous potassium permanganate was added until a test portion of the product remained pink for a few seconds, about 240 c.c. being required. The liquor was then filtered from manganese hydroxide, acidified with hydrochloric acid, and extracted with ether. The ethereal extract amounted to 1·5 grams, and after digestion with a little warm water left 1·0 gram of *p*-acetylaminobenzoic acid, which melted at 260° (corr.). After recrystallisation from boiling water, the acid formed glistening needles having the same melting point. A specimen of the pure acid from another source and a mixture of the two melted at the same temperature. The identification was confirmed by analysis (Found: $C = 59\cdot9$; $H = 5\cdot2$; $N = 7\cdot8$. Calc.: $C = 60\cdot3$; $H = 5\cdot1$; $N = 7\cdot8$ per cent.) and by hydrolysis to *p*-amino-benzoic acid, which melted at 190° (corr.) alone or mixed with the acid resulting from the reduction of *p*-nitrobenzoic acid.

*Reduction of 2-Benzeneazoglyoxaline with Zinc Dust and Acetic Acid: Isolation of Glycocyamidine, Aniline, and 2-Amino-4-*p*-aminophenylglyoxaline.*

To a boiling solution of 17·2 grams of 2-benzeneazoglyoxaline in 100 c.c. of glacial acetic acid and 300 c.c. of water, 45 grams of zinc dust were added gradually in the course of twenty minutes without further heating. The excess of zinc was removed, the liquor diluted with 2 litres of water, giving an indigo-coloured solution, and treated with hydrogen sulphide. After collecting the zinc sulphide—which had carried down the colouring matter—the liquor was mixed with 20 c.c. of hydrochloric acid and evaporated to dryness. The residue was dissolved in a little water, mixed with sodium carbonate, and extracted with ether, when 2·7 grams of insoluble, black material were deposited; this contained zinc

carbonate and the carbonate of 2-amino-4-*p*-aminophenylglyoxaline.
The ethereal extract left on evaporation 7·0 grams of practically
pure aniline.   The alkaline liquor was acidified faintly with hydro-
chloric acid, mixed with a solution of 23 grams of picric acid in
1 litre of boiling water, and stirred, when 2·6 grams of 2-amino-
4-*p*-aminophenylglyoxaline dipicrate separated immediately as a
brownish-yellow, crystalline powder which melted at 240°; for the
identification of this substance, the hydrochloride and base were
prepared and found to have the properties recorded above.

The filtrate from this salt was kept overnight, when 21·5 grams
of a granular, crystalline picrate, melting at 196°, separated, and
on concentrating the mother liquor a further 4·8 grams, melting at
180°, were obtained.   These crops were mixed, converted into the
hydrochloride, and crystallised from alcohol, when eventually 5·9
grams of pure glycocyamidine hydrochloride were obtained, that is,
43 per cent. of the theoretical yield.   It formed clusters of pris-
matic needles, which began to darken and sinter at 205° and
melted at 211—213° (corr.).   E. Schmidt (*Arch. Pharm.*, 1913,
251, 557) states that it begins to discolour at 200° and melts at
208—210°   (Found: C = 26·5;   H = 4·4;   N = 30·6;   Cl = 26·3.
$C_3H_5ON_3,HCl$. (135·6)   requires   C = 26·6;   H = 4·5;   N = 31·0;
Cl = 26·2 per cent.).

To complete the identification of this compound, the base and
some other salts were prepared.   The base crystallised from water
in colourless, prismatic needles, which began to darken slowly from
about 220° and quickly from about 250°, without melting even at
300°.   It was anhydrous.   (Found: C = 36·4; H = 4·8; N = 42·3.
$C_3H_5ON_3$ (99·1) requires C = 36·3; H = 5·1; N = 42·4 per cent.)
E. Schmidt (*loc. cit.*) states that glycocyamidine darkens from 220°,
but does not melt at 250°.   It gave with sodium nitroprusside and
sodium hydroxide an orange solution, which became Burgundy-red
on the addition of acetic acid (Weyl's reaction).   It is stable
towards cold aqueous permanganate in acid solution, but reduces
cold alkaline permanganate, yielding a green solution.

The platinichloride was obtained on spontaneous evaporation of
an aqueous solution in large, transparent, quadrilateral tablets
having the composition $C_3H_5ON_3,H_2PtCl_6,2H_2O$.   It begins to
darken at 220°, gradually sinters, and is quite black by 260° with-
out actually melting even at 300°.   E. Schmidt (*loc. cit.*) found
that glycocyamidine platinichloride had this composition and did
not melt at 260°, but sintered and blackened earlier.

The platinichloride was also obtained in an anhydrous form by
crystallisation from a hot concentrated solution, when it formed
clusters of prisms.

The additive compound with gold chloride, $C_3H_5ON_3,AuCl_3$, melted at 157—158° (corr.). Korndörfer (*Arch. Pharm.*, 1904, **242**, 633) found that glycocyamidine gold chloride had this composition, and melted at 153—154°.

The picrate crystallised from water in glistening, striated, yellow leaflets (flat needles) which melted at 215—216° (corr.). Jaffé (*Zeitsch. physiol. Chem.*, 1906, **48**, 430) describes glycocyamidine picrate as forming needles, which melt at 210°.

2- *and 4-p-Bromobenzeneazoglyoxaline.*

34·4 Grams of *p*-bromoaniline in 200 c.c. of hydrochloric acid and 600 c.c. of water were diazotised at $-2°$ to 0° by a solution of 14·4 grams of sodium nitrite in 72 c.c. of water. The solution was kept for twenty minutes and poured in a slow stream into a solution of 13·6 grams of glyoxaline and 300 grams of sodium carbonate crystals in 2 litres of water, previously cooled to 5°. After adding a little more aqueous sodium carbonate, the mixture was kept overnight, and the insoluble, yellow powder collected and washed with water. It amounted to 48·7 grams after drying in the air, decomposed at 245°, and was almost completely soluble in dilute hydrochloric acid. After fractional crystallisation from alcohol, there were obtained 37·5 grams of pure 2-p-*bromobenzeneazoglyoxaline* and 5·1 grams scarcely less pure, whilst the final mother liquors deposited a mixture of this compound with dark brown warts, which were separated mechanically, and amounted to about 2·5 grams, melting at about 175°. These were dissolved in dilute hydrochloric acid, and the solution was filtered from a little dark brown, insoluble matter and mixed with ammonia, when a yellow, gelatinous precipitate was formed, which readily became crystalline on warming and stirring. This base was collected and crystallised several times from alcohol, when 4-p-*bromobenzeneazoglyoxaline* was obtained in a pure state.

2-p-*Bromobenzeneazoglyoxaline* crystallises from alcohol in chestnut-brown, prismatic needles, which melt and decompose at 253° (**corr.**).

Found: $C = 42·9$; $H = 3·1$; $N = 22·1$.
$C_9H_7N_4Br$ (251·1) requires $C = 43·0$; $H = 2·8$; $N = 22·3$ per cent.

4-p-*Bromobenzeneazoglyoxaline* crystallises from alcohol in clusters of brownish-yellow prisms which melt and decompose at 191° (corr.).

Found: $C = 43·2$; $H = 3·1$; $N = 21·9$.
$C_9H_7N_4Br$ (251·1) requires $C = 43·0$; $H = 2·8$; $N = 22·3$ per cent.

On reducing this base (0·26 gram) with stannous chloride and distilling the resulting solution with an excess of sodium hydroxide, the volatile products consisted of *p*-bromoaniline (0·18 gram) and ammonia, which gave 0·05 gram of ammonium chloride.

Reduction of 2-p-Bromobenzeneazoglyoxaline with Stannous Chloride: Isolation of 2-Aminoglyoxaline, p-Bromoaniline, Guanidine, 2-Amino-4-p-aminophenylglyoxaline, and a Base, $C_9H_9N_4Br$.

To 78 grams of 2-*p*-bromobenzeneazoglyoxaline suspended in 40 c.c. of hydrochloric acid and 1 litre of boiling water, 400 c.c. of stannous chloride solution were added. The solution immediately became decolorised, and, after the removal of 0·5 gram of brown, insoluble matter, was concentrated under diminished pressure. The tin salts which separated were collected from time to time and combined, so that the product was obtained in two fractions, consisting of the crystalline tin salts and the syrupy residue.

The crystalline tin salts were dissolved in water and deprived of tin by hydrogen sulphide. The solution of hydrochlorides was evaporated to dryness, dissolved in a little water, and mixed with aqueous sodium carbonate, when 39·6 grams of *p*-bromoaniline separated. The filtrate from this gave a further 1·1 grams of the same compound on extraction with ether, and was next acidified with hydrochloric acid, evaporated to dryness, and extracted with absolute alcohol. (Insoluble material = *A*.) On distilling the alcohol, a brown syrup remained, which quickly crystallised and became a rock-like mass of 2-aminoglyoxaline hydrochloride, amounting to 15·8 grams and melting at 135—140°.

The syrupy tin salts were also dissolved in water and deprived of tin. The resulting solution was evaporated to dryness, dissolved in a little water, mixed with sodium carbonate, and extracted with ether. This, on concentration, deposited 0·9 gram of colourless needles, melting at 178° (corr.), which proved to be a *base* having the composition $C_9H_9N_4Br$ (compare p. 245). The ethereal mother liquor on evaporation left 2·5 grams of dark brown syrup which gradually crystallised, and consisted largely of *p*-bromoaniline.

The alkaline liquor was acidified with hydrochloric acid, evaporated to dryness under diminished pressure, and extracted with absolute alcohol. The insoluble salts, consisting mainly of sodium chloride, were combined with those obtained previously (*A*), dissolved in water, and mixed with aqueous picric acid, when 2·7 grams of 2-amino-4-*p*-aminophenylglyoxaline dipicrate, melt-

ing at 240°, separated; the identity of this salt was confirmed by its conversion into the hydrochloride and base. The alcoholic extract was evaporated under diminished pressure, and left 13·0 grams of brown syrup, which crystallised only partly on seeding with 2-aminoglyoxaline hydrochloride. It was converted into the stannichloride and crystallised fractionally from 10 per cent. hydrochloric acid, when 10·2 grams of 2-aminoglyoxaline stannichloride melting at 280° (corr.) were obtained. This is equivalent to 4·9 grams of 2-aminoglyoxaline hydrochloride, the total yield of which was therefore 20·7 grams, that is, 56 per cent. of the theoretical.

The remaining stannichlorides were not readily purified by fractional crystallisation, and were reconverted into hydrochlorides, which amounted to about 3 grams. This material was mixed with sodium carbonate, evaporated until nearly dry, and extracted with hot alcohol.* The extract was distilled and the residue mixed with an excess of 10 per cent. aqueous oxalic acid, when 1·6 grams of guanidine hydrogen oxalate separated in large crystals. After recrystallisation from water, this salt formed colourless spears, which melted at 173—174° (corr.) after drying at 100°, and was sparingly soluble in water.

It had the composition $CH_5N_3,C_2H_2O_4,H_2O$ previously recorded by Strecker (*Annalen*, 1861, **118**, 160). (Found: $H_2O = 10·3$. Calc.: $H_2O = 10·8$. Found, in dried salt, $C = 24·0$; $H = 4·9$; $N = 28·0$. Calc.: $C = 24·1$; $H = 4·7$; $N = 28·2$ per cent.) The melting point of a specimen of guanidine hydrogen oxalate prepared synthetically and that of a mixture of the two preparations was the same. The identification was confirmed by the preparation of the nitrate and picrate, which had the properties previously recorded.

The *base*, melting at 178° (corr.), obtained as a by-product in the above reaction (compare p. 244), forms colourless needles from alcohol or ether. It contains halogen. It is sparingly soluble in water, readily so in cold, and very easily soluble in hot alcohol, but sparingly so in ether. Its alcoholic solution gradually becomes purple when exposed to the air.

Found: $C = 43·0$; $H = 3·9$; $N = 21·9$.
$C_9H_9N_4Br$ (253·1) requires $C = 42·7$; $H = 3·6$; $N = 22·1$ per cent.

0·122 Gram mixed with an excess of hydrochloric acid and evaporated to dryness gave 0·153 gram of salt, which is therefore

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* The method employed for the extraction of guanidine carbonate is unsuitable, and it is probable that a considerable proportion remained behind with the sodium carbonate.

a *dihydrochloride* (calc. yield, 0·157 gram). This salt crystallised from water in elongated leaflets, which, after drying at 100°, melted and decomposed at 245° (corr.) after sintering earlier. The *(di)picrate* crystallises from water in woolly needles, which melt at 225° (corr.), and are sparingly soluble in hot, very sparingly so in cold water.

The base decolorises potassium permanganate instantly in cold dilute sulphuric acid solution, and gives a Burgundy-red coloration with sodium diazobenzene-*p*-sulphonate in aqueous sodium carbonate. When dissolved in dilute hydrochloric acid and mixed with sodium nitrite, it yields a colourless, crystalline precipitate, but the product—crystals and mother liquor—when poured into alkaline β-naphthol gives no coloration.

When an aqueous solution of the hydrochloride is mixed with sodium acetate and benzaldehyde, a turbid, yellow solution is produced—evidently owing to the formation of a benzylidene compound.

The composition and mode of formation of the base indicate that it is 2-*p*-bromobenzenehydrazoglyoxaline, or a substance resulting from this by the benzidine or semidine change. The formation of a dihydrochloride and a benzylidene derivative rule out the first suggestion, whilst the formation of the latter compound also eliminates the semidine-type formula III given below. This formula and the benzidine-type formula I are also incompatible with the behaviour of the compound on treatment with nitrous acid and sodium β-naphthoxide, but the semidine-type formula II, representing 2-5'-*bromo*-2'-*aminoanilinoglyoxaline*, admits the possibility of *o*-diazoimine formation with nitrous acid, and is in harmony with all the observed properties of the compound (compare p. 223).
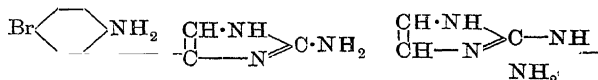
(I.)   (II.)
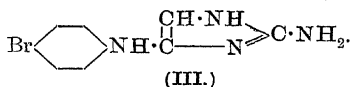
(III.)

2-Aminoglyoxaline (XII, p. 223).

For the purification of 2-aminoglyoxaline, crystallisation of the stannichloride and hydrogen oxalate has proved to be useful.

The free *base* can be obtained (1) from the hydrochloride by the

addition of an equivalent quantity of sodium carbonate, evaporation to dryness, and extraction with alcohol, and (2) from the hydrogen oxalate by treatment with aqueous barium hydroxide, removal of the excess of this by carbon dioxide, and evaporation of the solution under diminished pressure. In either case, it is obtained as a nearly colourless syrup which gradually turns brown on keeping. It is miscible with water and alcohol, sparingly soluble in chloroform, but hardly soluble in ether or benzene.

The *hydrochloride* crystallises from absolute alcohol in long, colourless plates which melt at 152° (corr.). It is deliquescent, and readily soluble in cold, very readily so in hot absolute alcohol. Its aqueous solution reacts neutral to litmus.

Found: $C = 30.2$; $H = 5.2$; $N = 34.7$; $Cl = 29.9$.
$C_3H_5N_3,HCl$ (119·5) requires $C = 30.1$; $H = 5.1$; $N = 35.1$; $Cl = 29.7$ per cent.

The *stannichloride* crystallises from two to two and a-half times its weight of 10 per cent. hydrochloric acid in prismatic needles, which are anhydrous and melt at 286° (corr.). It is readily soluble in water.

Found: $Cl = 42.4$.
$(C_3H_5N_3)_2,H_2SnCl_6$ (499·6) requires $Cl = 42.6$ per cent.

The *nitrate* separates from water in large, transparent tablets, which are anhydrous, and, after drying at 100°, sinter from about 125° and melt at 135—136° (corr.).

Found: $N = 38.2$.
$C_3H_5N_3,HNO_3$ (146·1) requires $N = 38.4$ per cent.

The *hydrogen oxalate* crystallises from water in large, colourless tablets, which are anhydrous and melt and effervesce at 211° (corr.). It is sparingly soluble in cold, readily so in hot water.

Found: $N = 24.0$.
$C_3H_5N_3,C_2H_2O_4$ (173·1) requires $N = 24.3$ per cent.

The *picrate* separates from water in long, glistening, silky needles, or in short, prismatic needles, both melting at 236° (corr.) after drying at 100°. It is sparingly soluble in cold, fairly readily so in hot water.

Reactions of 2-Aminoglyoxaline.—2-Aminoglyoxaline hydrochloride dissolved in dilute aqueous copper sulphate gives on the addition of sodium hydroxide a green precipitate, which rapidly darkens and becomes purple-brown. The same precipitate—evidently a copper salt—is obtained eventually with Fehling's solution; no reduction of this solution takes place even on boiling. 2-Aminoglyoxaline nitrate in aqueous silver nitrate gives a white

precipitate on the addition of ammonia; this precipitate is soluble in excess of ammonia, and the solution deposits metallic silver on heating.

2-Aminoglyoxaline hydrochloride in aqueous solution decolorises aqueous potassium permanganate instantly; with ferric chloride, it gives no coloration. With sodium diazobenzene-p-sulphonate in aqueous sodium carbonate, it gives a deep red colour. On the addition of sodium nitrite to aqueous 2-aminoglyoxaline hydrochloride, a clear, yellow solution is produced which gives a soluble, brownish cherry-coloured dye with β-naphthol in aqueous sodium hydroxide. An aqueous solution of 2-aminoglyoxaline hydrochloride mixed with dilute aqueous sodium nitroprusside gives, on the addition of sodium hydroxide, a deep blue colour, which slowly changes to a bright chestnut on keeping.

2-Aminoglyoxaline is very stable towards hot acids and alkalis. When boiled with 10 per cent. aqueous sodium hydroxide, no ammonia is evolved, and it can be recovered unchanged from the solution. It can be recovered mainly unchanged after heating with concentrated hydrochloric acid for three hours at 170°, and even after three hours at 200° a small proportion can be recovered, together with ammonium chloride and other unidentified products.

An aqueous solution of 2-aminoglyoxaline hydrochloride containing an excess of sodium acetate gives no coloration or other evidence of the formation of a benzylidene derivative when mixed with benzaldehyde.

2-Acetylaminoglyoxaline was prepared by boiling 2-aminoglyoxaline hydrochloride with anhydrous sodium acetate and acetic anhydride for one hour, and mixing the product with aqueous sodium carbonate. It crystallises from water in small prisms which melt to a brown liquid at 287° (corr.), after sintering and darkening from about 270°. It is anhydrous and sparingly soluble in cold water, but fairly readily so in hot water.

Found : C = 47·7 ; H = 5·7 ; N = 33·4.

$C_5H_7ON_3$ (125·1) requires C = 48·0 ; H = 5·6 ; N = 33·6 per cent.

The reactions of this substance are described with those of the next compound.

2-Benzoylaminoglyoxaline was prepared by the Schotten-Baumann method. The crude product collected from the reaction liquor appears to be a di- or tri-benzoylaminoglyoxaline. After washing with ether to remove benzoic anhydride, it formed a nearly colourless, crystalline powder, which contained only a trace of chloride, but gave an odour of benzoyl chloride when boiled with dilute hydrochloric acid. When treated with a little hot alcohol,

it dissolved, and 2-benzoylaminoglyoxaline crystallised from the hot liquor, whilst the mother liquor from this left an oil—apparently ethyl benzoate—on distillation. 2-Benzoylaminoglyoxaline was purified by crystallisation from alcohol, from which it separates in glistening leaflets, melting at 227° (corr.) after sintering earlier. It is sparingly soluble even in hot alcohol, and almost insoluble in boiling water.

Found: C = 63·9; H = 4·9; N = 22·4.

$C_{10}H_9ON_3$ (187·1) requires C = 64·1; H = 4·9; N = 22·5 per cent.

2-Acetylaminoglyoxaline and 2-benzoylaminoglyoxaline are soluble in dilute hydrochloric acid and in aqueous sodium hydroxide, but not in aqueous sodium carbonate. They give cherry-red solutions with sodium diazobenzene-p-sulphonate in sodium carbonate, but do not give colorations with sodium nitroprusside and sodium hydroxide. They do not change the colour of cold aqueous acid permanganate, but give green solutions with cold aqueous permanganate in sodium hydroxide solution. When mixed with hydrochloric acid and sodium nitrite, they do not couple with β-naphthol in aqueous sodium hydroxide.

The Benzeneazo-4-methylglyoxalines.

37·2 Grams of aniline in 100 c.c. of hydrochloric acid and 300 c.c. of water were diazotised with 28·8 grams of sodium nitrite in 150 c.c. of water. The solution was run slowly into a solution of 32·8 grams of 4-methylglyoxaline and 100 grams of sodium hydrogen carbonate in 2 litres of water at 10° and kept overnight. The orange precipitate was collected, washed well with water (filtrate F), and triturated successively with 500, 250, and 250 c.c. of 2·5 per cent. aqueous hydrochloric acid. The insoluble fraction formed a dark red powder, which amounted to 23·2 grams, and decomposed at 175° after sintering from 160°. On crystallisation from 300 c.c. of alcohol, it gave 17·3 grams of pure 2:5-*bisbenzene-azo-4-methylglyoxaline*, the remainder of the material forming a black resin.

The hydrochloric acid extract was basified with sodium carbonate, and gave 40·4 grams of a yellow, crystalline powder, which sintered from 160° and decomposed at 195°. On crystallisation from 400 c.c. of alcohol, it gave, successively, 13·1 grams melting at 235°, 3·9 grams melting at 232°, which both gave 5-*benzeneazo-4-methylglyoxaline* on recrystallisation, then 7·4 grams melting at 175°, which gave 2-*benzeneazo-4-methylglyoxaline* on recrystallisation, then 12·4 grams of a mixture of the two compounds.

Owing to the formation of the bis-compound in the above reaction, the benzenediazonium chloride employed was insufficient to combine with the whole of the methylglyoxaline present, and it was calculated that 10·5 grams of this remained in the filtrate F. This was accordingly treated with a diazo-solution prepared from 11·9 grams of aniline, and gave further quantities of the substances described above, 5·3 grams of the bis-compound and 5·6 grams of 5-benzeneazo-4-methylglyoxaline being obtained in a nearly pure state.

2-Benzeneazo-4-methylglyoxaline (XIV, p. 224) crystallises from alcohol in orange prisms, which melt at 185° (corr.).

Found : C=64·8 ; H=5·6 ; N=30·1.

$C_{10}H_{10}N_4$ (185·2) requires C=64·5 ; H=5·4 ; N=30·1 per cent.

5-Benzeneazo-4-methylglyoxaline (XVIII, p. 224) crystallises from alcohol in flat, glistening, copper-coloured needles, which melt and decompose at 240° (corr.).

Found : C=64·5 ; H=5·6 ; N=30·0.

$C_{10}H_{10}N_4$ (185·2) requires C=64·5 ; H=5·4 ; N=30·1 per cent.

2 : 5-Bisbenzeneazo-4-methylglyoxaline separates from alcohol in prismatic needles and from ethyl acetate in cubes. Both forms are garnet-red in colour and melt and decompose at 206° (corr.).

Found : C=66·0, 65·9 ; H=5·1, 5·1 ; N=28·8, 28·8.

$C_{16}H_{14}N_6$ (290·2) requires C=66·2 ; H=4·9 ; N=29·0 per cent.

This substance is readily soluble in alcohol, ethyl acetate, or acetone, fairly readily so in chloroform, but sparingly so in ether or benzene.

It is soluble in aqueous sodium hydroxide, and is reprecipitated unchanged on the addition of acetic acid. It is only very sparingly soluble in dilute hydrochloric acid. When boiled with 10 per cent. aqueous hydrochloric acid, it is quickly resinified with effervescence, doubtless due to nitrogen, and the production of an odour of phenol.

Reduction of 2-Benzeneazo-4-methylglyoxaline with Stannous Chloride.

1·5 Grams of 2-benzeneazo-4-methylglyoxaline gave 1·4 grams of 2-amino-5-*p*-aminophenyl-4-methylglyoxaline dihydrochloride when reduced with stannous chloride in the manner previously described for the lower homologue (p. 238).

2-Amino-5-p-aminophenyl-4-methylglyoxaline dihydrochloride crystallises from water in diamond-shaped plates, which are anhydrous and do not melt below 300°. It is readily soluble in cold, very readily so in hot water.

Found: C=46·0, 45·9; H=5·5, 5·5.

$C_{10}H_{12}N_4,2HCl$ (201·0) requires C=46·0; H=5·4 per cent.

When boiled with an excess of aqueous sodium carbonate and animal charcoal, it yields the *monohydrochloride*, unlike the lower homologue, which yields the corresponding base under this treatment.

The *monohydrochloride* crystallises from alcohol in flat needles which sinter at about 80°, become discoloured rapidly about 240°, and melt at 260° (corr.). It is readily soluble in hot water or alcohol, less so in these solvents when cold.

Found, in air-dried base, loss at 60° in a vacuum, 13·2, 13·3.

$C_{10}H_{12}N_4,HCl,2\frac{1}{2}H_2O$ requires loss of $2H_2O=13·4$ per cent.

Found, in base so dried: C=51·5; H=5·6; N=24·0, 24·0; Cl=14·9.

$C_{10}H_{12}N_4,HCl,\frac{1}{2}H_2O$ (233·7) requires C=51·4; H=6·0; N=24·0; Cl=15·2 per cent.

The *dipicrate* forms glistening, yellow needles, which melt and decompose at 255° (corr.) after darkening earlier. It is very sparingly soluble even in boiling water.

An aqueous solution of the hydrochloride reduces cold ammoniacal silver nitrate. It gives, with Fehling's solution, a greyish-green precipitate, which becomes pale brown on boiling the liquor; with cold aqueous acid permanganate, instant reduction; with sodium diazobenzene-*p*-sulphonate, a pale orange colour, which deepens on keeping; with hydrochloric acid and sodium nitrite, an orange-yellow solution, which yields a sparingly soluble claret dye when added to a solution of β-naphthol in aqueous sodium hydroxide. On the addition of sodium hydroxide to an aqueous solution of the hydrochloride and sodium nitroprusside, an orange colour is produced, which changes to green on the addition of acetic acid.

The *diacetyl* derivative was prepared by the action of sodium acetate and acetic anhydride on the dihydrochloride, and was purified by crystallisation of the hydrochloride.

2-Acetylamino-5-p-acetylaminophenyl-4-methylglyoxaline hydrochloride crystallises from water in felted, silky needles, which are sparingly soluble in cold water, contain $4H_2O$, and, after drying at 100°, melt and decompose at 303° (corr.).

Found, in air-dried salt, loss at 100°=19·0.

$C_{14}H_{16}O_2N_4,HCl,4H_2O$ requires $H_2O=18·9$ per cent

Found, in salt dried at 100°, Cl=11·4.

$C_{14}H_{16}O_2N_4,HCl$ (308·7) requires Cl=11·5 per cent.

On adding ammonia to an aqueous solution of the hydrochloride, the base was precipitated in minute, glistening needles, which, after drying at 100°, melted to a red liquid at 280° (corr.).

Monobenzylidene Derivative.—To 0·5 gram of the dihydrochloride in 5 c.c. of water there were added, first, 0·55 gram of sodium acetate in 5 c.c. of water, and then 0·5 c.c. of benzaldehyde, and the mixture was stirred. A yellow colour was developed, and the aqueous liquor became turbid and gradually deposited crystals. On adding a few drops of acetic acid and ether, the quantity of crystals was increased. They were collected and washed with water and ether, when there remained 0·5 gram of a pale yellow, crystalline powder, which proved to be the *acetate* of 2-*amino*-5-*p-benzylideneaminophenyl-4-methylglyoxaline*. When dried at 100°, it melts and decomposes at 208° (corr.), after sintering and darkening earlier.

Found, in substance dried in a vacuum, $C = 67·2$; $H = 6·2$; $N = 16·2$.[*]

$C_{17}H_{16}N_4,C_2H_4O_2$ (336·3) requires $C = 67·8$; $H = 6·0$; $N = 16·7$ per cent.

This salt is very sparingly soluble in cold water, but slightly so in boiling water, with which, however, it gives an odour of benzaldehyde, and thus appears to suffer hydrolysis. When mixed with aqueous sodium carbonate, it yields the base as a deep yellow, insoluble gum, which could not be obtained in crystalline form. When the acetate is moistened with 10 per cent. aqueous hydrochloric acid, it turns red, but does not dissolve until the mixture is warmed, when the red colour disappears.

Reduction of 2-Benzeneazo-4-methylglyoxaline with Zinc Dust and

Two grams of the azo-compound were reduced by the method applied to the lower homologue (p. 241) and worked up in the same manner as far as the removal of the aniline by extraction with ether. The solvent removed 0·65 gram of crude aniline. The alkaline liquor remaining was acidified with hydrochloric acid, evaporated to dryness, and extracted with absolute alcohol, when 1·4 grams of brown syrup were removed. This, when dissolved in a little absolute alcohol and kept, deposited 0·7 gram of nearly pure alacreatinine hydrochloride.

This was converted into the picrate, when a very small quantity of 2-amino-5-*p*-aminophenyl-4-methylglyoxaline dipicrate separated

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[*] The substance left a trace of ash on combustion.

from the hot solution, whilst, on cooling, alacreatinine picrate crystallised out. After recrystallisation, the salt was obtained in a pure state, and was converted into the base and hydrochloride by the usual methods.

Alacreatinine crystallises from water in stout, elongated prisms which resemble carbamide, and contain $1H_2O$, as previously stated by Baumann (*Annalen*, 1873, **167**, 83). After drying at 100°, it melts at 222—223° (corr.). (Found, in air-dried salt, $H_2O = 13.6$. Calc.: 13.7. Found, in dried salt, $C = 42.4$; $H = 6.3$; $N = 36.9$. Calc.: $C = 42.5$; $H = 6.2$; $N = 37.1$ per cent.)

It does not give Weyl's reaction, and does not reduce cold aqueous acid permanganate, but gives a green solution with cold alkaline permanganate.

The *hydrochloride* crystallises from absolute alcohol in clusters of prisms, which are anhydrous and melt at 202—203° (corr.). It is very readily soluble in water, sparingly soluble in cold, fairly readily so in hot alcohol.

Found: $Cl = 23.6$.

$C_4H_7ON_3,HCl$ (149.6) requires $Cl = 23.7$ per cent.

The *picrate* separates from water in yellow, prismatic needles, which are anhydrous and melt and decompose at 212° (corr.) after sintering from about 200°. It is sparingly soluble in cold, fairly readily so in hot water.

Found: $N = 24.5$.

$C_4H_7ON_3,C_6H_3O_7N_3$ (342.2) requires $N = 24.6$ per cent.

Reduction of 5-Benzeneazo-4-methylglyoxaline with Stannous Chloride.

Fourteen grams of the azo-compound were dissolved in a boiling mixture of 70 c.c. of 10 per cent. aqueous hydrochloric acid and 140 c.c. of water, and mixed with 80 c.c. of stannous chloride solution. The crystalline and residual tin salts were separated as in the experiments described earlier, and decomposed separately by hydrogen sulphide. The crystalline salts gave a solution of hydrochlorides, which, when evaporated nearly to dryness and mixed with alcohol, left 6.1 grams of ammonium chloride undissolved. (Alcoholic mother liquor = A.) The residual salts gave a solution of hydrochlorides, which on concentration deposited $1.7 + 0.5$ grams of the *hydrochloride*, $C_9H_{10}ON_2,HCl$, described below, and on further concentration and addition of alcohol gave 1.5 grams of ammonium chloride. The alcoholic mother liquor was combined

with *A*, and gave 4·7 grams of aniline, together with 3·8 grams of a brown, gummy, hydrochloride. This was a mixture from which only very small quantities of crystalline compounds were isolated by various methods of treatment.

The *hydrochloride*, $C_9H_{10}ON_2,HCl$, crystallises from water in colourless, transparent, rectangular tablets, which melt and effervesce at 308° (corr.) after sintering and darkening earlier. It is readily soluble in hot, less so in cold water, giving a solution which is strongly acid to litmus.

Found, in air-dried salt, loss at 110° = 1·7.

Found, in salt dried at 110°: C = 54·8, 54·8, 55·0; H = 5·9, 5·0, 5·2; N = 13·5; Cl = 17·2.

$C_9H_{10}ON_2,HCl$ (198·6) requires C = 54·4; H = 5·6; N = 14·1; Cl = 17·8 per cent.

The corresponding *base* is obtained by adding ammonia to a concentrated aqueous solution of the hydrochloride. It crystallises from water in brilliant, elongated prisms, which are anhydrous and melt at 185° (corr.).

Found: C = 66·6, 66·1; H = 6·2, 6·1; N = 17·8, 17·2.

$C_9H_{10}ON_2$ (162·1) requires C = 66·6; H = 6·2; N = 17·3 per cent.

The base is more readily soluble in dilute aqueous sodium hydroxide than in water. With silver nitrate it yields a white precipitate, which dissolves on the addition of ammonia; on boiling this solution, no reduction takes place. The base does not reduce Fehling's solution on boiling.

It is stable towards cold aqueous acid potassium permanganate, but slowly reduces cold alkaline permanganate, giving a green solution. It gives no coloration with sodium diazobenzene-*p*-sulphonate in aqueous sodium carbonate. When dissolved in hydrochloric acid and mixed with sodium nitrite, it fails to couple with β-naphthol in aqueous sodium hydroxide. The hydrochloride is recovered slightly charred, but otherwise unchanged, after the action of concentrated hydrochloric acid at 170° for two and a-half hours.

The quantity of this compound available was insufficient for the determination of its constitution, and we are consequently unable to offer any suggestion as to how one of the carbon atoms of the starting material has been eliminated. It is perhaps worth recording that the formula $C_9H_{10}ON_2$ is that of a phenyldihydroglyoxalone.

Reduction of 5-Benzeneazo-4-methylglyoxaline with Zinc Dust and Acetic Acid.

Ten grams of the azo-compound were dissolved in 150 c.c. of boiling 50 per cent. acetic acid and reduced by adding gradually 16 grams of zinc dust. After removing the zinc as sulphide, the liquor was mixed with 20 c.c. of hydrochloric acid, evaporated to a syrup, and mixed with alcohol, when 1·3 grams of ammonium chloride were collected. The alcoholic mother liquor was deprived of the solvent, dissolved in water, mixed with sodium carbonate, and shaken with ether, when 1·6 grams of the base, $C_{10}H_{11}ON_3$, described below, separated as a nearly colourless, insoluble, crystalline powder. The ethereal solution left on evaporation 3·3 grams of aniline. From the alkaline liquor, 5·5 grams of a mauve varnish were obtained, from which only small quantities of crystalline substances could be isolated by various methods of treatment.

The *base*, $C_{10}H_{11}ON_3$, crystallises from water in small, colourless, glistening, rhomboidal plates, which are anhydrous and melt at 265° (corr.). It is very sparingly soluble in cold water, rather more readily in boiling water.

Found: C = 63·7; H = 6·2; N = 22·0.

$C_{10}H_{11}ON_3$ (189·2) requires C = 63·5; H = 5·9; N = 22·2 per cent.

The *hydrochloride* crystallises from absolute alcohol in transparent, oblong plates which melt at· 206—208° (corr.). It is readily soluble in water, concentrated hydrochloric acid, or hot alcohol. Its aqueous solution reacts strongly acid to litmus.

The base dissolves slowly in cold 10 per cent. aqueous sodium hydroxide, readily on warming, and a well-crystallised sodium salt separates from the solution in prismatic needles. This salt is decomposed by carbon dioxide with the regeneration of the base. A solution of the base in aqueous sodium hydroxide gives with Fehling's solution no change in the cold, but a green precipitate on boiling. A solution· of the base in nitric acid gives no precipitate with silver nitrate, but on the addition of ammonia a white precipitate, which dissolves on heating the solution, reappears on cooling, and is soluble in excess of ammonia. An aqueous solution of potassium permanganate is unaffected by a solution of the base in sulphuric acid, but turns green with a solution of the base in aqueous sodium hydroxide. The base does not couple with sodium diazobenzene-*p*-sulphonate in aqueous sodium carbonate, and when dissolved in hydrochloric acid and mixed with sodium nitrite does not couple with sodium β-naphthoxide.

When the hydrochloride is heated with concentrated hydrochloric

acid for two and a-half hours at 170°, it is decomposed, with the formation of ammonium chloride and a hydrochloride, which crystallises from alcohol in plates, melting and decomposing at about 280° (corr.).

4-Benzeneazo-2-methylglyoxaline.

This was prepared by the action of benzenediazonium chloride on 2-methylglyoxaline in aqueous sodium carbonate. The crude product readily resinified when boiled with alcohol, and only a small proportion was obtained in a pure state. It forms brick-red prisms, which melt at 158° (corr.) and are very readily soluble in alcohol.

Found : C = 64·3 ; H = 5·7 ; N = 30·0.
$C_{10}H_{10}N_4$ (186·2) requires C = 64·5 ; H = 5·4 ; N = 30·1 per cent.

4-p-Bromobenzeneazo-2-methylglyoxaline.

This was prepared in good yield by the action of p-bromo-benzenediazonium chloride on 2-methylglyoxaline in aqueous sodium carbonate. It crystallises from absolute alcohol in red, rhomboidal prisms, which are anhydrous and melt and decompose at 200° (corr.).

Found : N = 21·0.
          $C_{10}H_9N_4Br$ (265·1) requires N = 21·1 per cent.

From ordinary alcohol, it separates in elongated prisms, which lose 2·2 per cent. of water at 60° in a vacuum. This hydrated form melts at about 135° when heated quickly, and softens at this temperature when heated slowly, finally melting at about 190°. It can be dehydrated by crystallisation from absolute alcohol.

The reduction of this compound with either stannous chloride or zinc dust and acetic acid led to mixtures of products, from which no crystalline compounds except p-bromoaniline and ammonium chloride could be isolated.

2-Phenyl-4-p-bromobenzeneazoglyoxaline.

8·6 Grams of p-bromoaniline were diazotised and the liquor added to 7·2 grams of 2-phenylglyoxaline and 70 grams of hydrated sodium carbonate in 4 litres of water at 8°, the solution being vigorously stirred during the addition. Separation of an orange

precipitate began at once, but was not complete until forty-eight hours had elapsed. The crude product was crystallised from alcohol, and gave 13 grams of the pure azo-compound.

2-*Phenyl*-4-p-*bromobenzeneazoglyoxaline* crystallises from alcohol in clusters of fine, orange needles, which melt at 201° (corr.), and are anhydrous.

Found: $N = 16.9$.

$C_{15}H_{11}N_4Br$ (327·1) requires $N = 17.1$ per cent.

Reduction of 2-Phenyl-4-p-bromobenzeneazoglyoxaline with Stannous Chloride: Formation of a Base, $C_{15}H_{13}N_4Br$.

Two grams of the azo-compound were suspended in 20 c.c. of boiling 5 per cent. aqueous hydrochloric acid and mixed with 10 c.c. of stannous chloride solution. The solution was filtered quickly from a little resinous matter and mixed with 20 c.c. of concentrated hydrochloric acid, when a crystalline tin salt separated. This was deprived of tin, and the filtrate was evaporated to a small volume, when 0·85 gram of a crystalline hydrochloride separated.

This *hydrochloride* crystallises from dilute hydrochloric acid in nearly colourless needles, which, after drying in a vacuum, melt and decompose at 255° (corr.).

Found: $C = 45.0$; $H = 3.8$; $N = 13.7$.
$C_{15}H_{13}N_4Br,2HCl$ (402·0) requires $C = 44.8$; $H = 3.8$; $N = 13.9$
per cent.

0·1530 gave, by Carius's method, 0·1750 $AgCl + AgBr$. Calc., 0·1806.

It is sparingly soluble in cold water, more readily so in hot water. The aqueous solution gradually acquires a purple colour in the air or on the addition of acidified aqueous potassium permanganate. In the presence of an excess of hydrochloric acid, aqueous solutions are stable in the air. Sodium carbonate or ammonia precipitate the base as a grey, flocculent precipitate which is soluble in ether, the ethereal solution rapidly assuming a purple colour. On the addition of sodium hydroxide to an aqueous solution of the hydrochloride, a pale purple solution results. On adding sodium diazobenzene-*p*-sulphonate to a dilute solution of the compound in the presence of sodium carbonate, a dull purple colour is produced. An aqueous solution of the hydrochloride containing an excess of hydrochloric acid gives on the addition of

sodium nitrite a deep orange solution, which yields a sparingly
soluble purple dye with sodium β-naphthoxide. On mixing a solu-
tion of the hydrochloride in dilute acetic acid with sodium acetate
and benzaldehyde, there is evidence of the formation of a benzyl-
idene derivative. When an aqueous solution of the hydrochloride
is mixed with sodium nitroprusside, a pale buff precipitate is
formed, which dissolves in sodium hydroxide, giving a deep red
solution.

The *triacetyl* derivative was obtained by heating the hydro-
chloride for one hour on the water-bath with an excess of acetic
anhydride and anhydrous sodium acetate. On heating the product
with aqueous sodium carbonate, it separated as a slate-grey, crystal-
line powder, which did not melt at 300°.

Found : C = 55·2 ; H = 4·1 ; N = 12·6, 12·7 ; Br = 17·3.
$C_{21}H_{19}O_3N_4Br$ (455·2) requires C = 55·4 ; H = 4·2 ; N = 12·3 ;
Br = 17·6 per cent.

It is almost insoluble in boiling water or alcohol, and does not
dissolve in dilute acids or in aqueous sodium hydroxide.

From its mode of formation, composition, and properties, **it** is
clear that the hydrochloride, $C_{15}H_{13}N_4Br,2HCl$, arises from
2-phenyl-4-*p*-bromobenzenehydrazoglyoxaline by a change of the
semidine or benzidine type, but it is not possible to decide definitely
without further evidence which of the three formulæ given below
represents its constitution.

2-p-*Sulphobenzeneazoglyoxaline*-4 : 5-*dicarboxylic Acid*
(XX, p. 226).

20·8 Grams of sulphanilic acid were converted into diazobenzene-
p-sulphonic acid, and the moist crystals (representing about
20 grams of dry substance) were added to a cold solution of 16
grams of glyoxaline-4 : 5-dicarboxylic acid in 240 c.c. of 10 per
cent. aqueous sodium hydroxide. After keeping for one and a-half
hours, the liquor was mixed with sufficient glacial acetic acid
(36 c.c.) to neutralise the alkali, cooled, and kept for half an hour,
when a mass of silky, yellow needles—the disodium salt of the new

acid, separated. These were recrystallised twice from 200 c.c. of water, and finally dissolved in 150 c.c. of hot water and mixed with 50 c.c. of hydrochloric acid, when 12 grams of 2-*p*-sulphobenzene-azoglyoxaline-4:5-dicarboxylic acid separated in red, microscopic prisms mixed with some smaller crystals of glyoxaline-4:5-dicarb-oxylic acid, from which it was purified by fractional crystallisation from water.

The acid separates from water with $2H_2O$, which is lost at 130° in a vacuum, but not at 100—110° under normal pressure.

Found, in air-dried substance, loss at 130° in a vacuum = 10·0; C = 35·5; H = 3·3; N = 15·1; S = 8·2.

$C_{11}H_8O_7N_4S,2H_2O$ (376·2) requires $H_2O = 9·6$; C = 35·1; H = 3·3; N = 14·9; S = 8·5 per cent.

It is sparingly soluble in cold water, but readily so in hot. It is soluble in aqueous alkalis, but not more soluble in dilute aqueous mineral acids than in water.

The *disodium* salt separates in yellow, silky needles, which contain $3H_2O$, when the acid is dissolved in aqueous sodium hydroxide and sufficient acetic acid is added to combine with the alkali. It is readily soluble in hot water, somewhat sparingly so in cold.

Found, in air-dried salt, loss at 100° = 11·6, 12·6.

$C_{11}H_6O_7N_4SNa_2,3H_2O$ (438·2) requires $3H_2O = 12·3$ per cent.

Found, in salt dried at 100°, S = 8·2; N = 11·7.

$C_{11}H_6O_7N_4SNa_2$ (384·2) requires S = 8·4; N = 12·0 per cent.

Reduction of 2-p-Sulphobenzeneazoglyoxaline-4:5-dicarboxylic Acid: Formation of 2-Aminoglyoxaline-4:5-dicarboxylic Acid (XXI, p. 226).

6·2 Grams of the disodium salt were dissolved in 60 c.c. of 10 per cent. aqueous sodium hydroxide, mixed with 12 grams of sodium hyposulphite (80 per cent.), and boiled. The nearly colourless solution was kept overnight, acidified with hydrochloric acid, boiled, and filtered hot, when 1·6 grams of crude 2-aminoglyoxaline-4:5-dicarboxylic acid separated. This was purified by solution in aqueous sodium hydroxide, filtration, and reprecipitation with hydrochloric acid, and finally crystallised from about 500 c.c. of dilute hydrochloric acid.

2-Aminoglyoxaline-4:5-dicarboxylic acid forms minute, pale buff needles, which effervesce at 245° (corr.) and then melt. It is very sparingly soluble in cold water, a little more readily in hot.

Found, in substance dried at 110°, C = 34·6; H = 3·2; N = 24·6.
$C_5H_5O_4N_3$ (171·1) requires C = 35·1; H = 3·0; N = 24·6 per cent.

It is soluble in aqueous alkalis, but not appreciably more soluble in dilute acids than in water. An aqueous solution, acidified with sulphuric acid, decolorises cold aqueous permanganate instantly. When treated with hydrochloric acid and sodium nitrite and poured into a solution of β-naphthol in aqueous sodium hydroxide, it gives a reddish-brown colour. With sodium diazobenzene-*p*-sulphonate in aqueous sodium carbonate, it gives a reddish-brown colour. It does not give any characteristic colour with sodium nitroprusside and sodium hydroxide.

Action of Water at 170°.—After a preliminary experiment, in which it was found that the product contained ammonium carbonate, 1·33 grams of the acid and 30 c.c. of water were heated in a sealed tube for twelve hours at 170°, when a dark brown deposit formed. After adding alkali and distilling into standard acid, 0·157 gram of ammonia was found, whereas 0·132 gram represents the liberation of one molecular proportion. From the residue of the distillation, small quantities of a crystalline picrate were isolated, but in insufficient amount for characterisation.

Action of Boiling Aniline.—0·9 Gram of the acid was boiled with 10 c.c. of aniline for six hours under a reflux condenser, in which a small quantity of ammonium carbonate collected. The product was distilled with steam to remove aniline, and left a pale brown, aqueous liquor containing some resinous matter. The liquor was cooled, filtered, and mixed with cold saturated aqueous picric acid, when 1·0 gram of a crystalline picrate, melting at about 215°, was obtained. After crystallising this from water twice, it gave 0·4 gram of 2-aminoglyoxaline picrate, melting at 234° (corr.), the pure substance melting at 236°, and a mixture of the two at 234° in the same bath. From the picrate, the hydrochloride and stannichloride were prepared, and identified as the salts of 2-aminoglyoxaline previously described.

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XXVII.—*Mercury   Mercaptide   Nitrites   and   their Reaction with the Alkyl Iodides.   Part IV.   Chain Compounds of Sulphur* (continued).

By Prafulla Chandra RâY and Prafulla Chandra Guha.

In this investigation, the reactions of several actual and potential mercaptans, some of them cyclic, have been studied. It was expected that in these, the molecules being of a more complex nature, the radicle, especially ·$SHgNO_2$, would far more readily part company with the parent substance and lead an independent existence as the compound, $3(SHgNO_2),HgO$ (T., 1917, **111**, 101).   The result has proved to be just the reverse.

5-Thiol-2-thio-3-phenyl-2 : 3-dihydro-1 : 3 : 4-thiodiazole,

$$\begin{matrix} N Ph\cdot N \\ C S - S \end{matrix} \!\!> C\cdot SH,$$
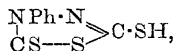
yields, with mercuric nitrite, the corresponding mercaptide nitrite (compare T., 1916, **109**, 131),

$$RSH + Hg(NO_2)_2 = RS\cdot HgNO_2 + HNO_2.$$
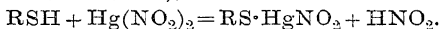
Mercuric nitrite and phenyl mercaptan furnish a compound, Ph_2S_3Hg, evidently a mercaptide, and sometimes another oxy-salt, $(3PhS,HgO)_2$. It is only in exceptional cases (see p. 264) that the expected mercaptide nitrite, $PhS\cdot HgNO_2$, is obtained, and then only in an impure form.

The reaction appears to proceed in the following stages:

$$PhSH + Hg(NO_2)_2 = PhS\cdot HgNO_2 + HNO_2.$$
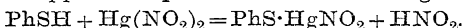
The nitrous acid thus liberated oxidises another pair of molecules of phenyl mercaptan to diphenyl disulphide, and the latter then forms with mercuric nitrite the compound,

$$\begin{matrix} PhS\cdot SPh \\ \diagup \quad \diagdown \\ O_2NHg \quad NO_2 \end{matrix} \xrightarrow{\;N_2O_3\;} \begin{matrix} PhS\cdot SPh \\ \diagup \quad \diagdown \\ Hg - O \end{matrix}$$
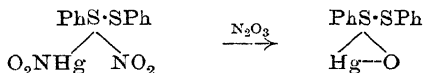
Two molecules of this compound combine with a molecule of diphenyl disulphide, giving rise to the compound,

$$2\; \begin{matrix} PhS\cdot SPh \\ \diagup \quad \diagdown \\ Hg - O \end{matrix} \;,Pb_2S_2.$$
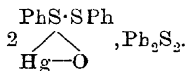
3-Phenyl-5-methyl-2-thiohydantoin gives the mercaptide nitrite,

$$\begin{matrix} CO - NPh \\ CHMe\cdot N \end{matrix} \!\!> C\cdot SHgNO_2.$$
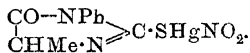
Potential Mercaptans.

The interaction of mercuric nitrite and the aryl substituted thiocarbamides, thiosemicarbazides, thiocarbazides, etc., follows the ordinary course, but no detachment of the organic radicle takes place. Thus with phenylthiocarbamide we have

$$\text{NHPh·C(NH}_2\text{):S} \xrightarrow{\text{Hg(NO}_2)_2} \text{NHPh·C(:NH)·S·HgNO}_2 \longrightarrow$$
$$\text{NHPh·C(:NH)·S(HgNO}_2)\!\!<^{\text{Hg}}_{\text{O}}.$$
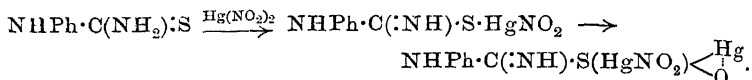
Attention may also here be directed to the interesting analogous case of potassium phenyldithiocarbazinate, which combines in itself the function of a real and of a potential mercaptan, thus:

$$\text{NHPh·NH·CS}_2\text{K} \xrightarrow{\text{Hg(NO}_2)_2} \text{NHPh·N:C(SH)·SK} \longrightarrow$$
$$\text{NHPh·N:C(S·HgNO}_2)·S(HgNO}_2)\!\!<^{\text{Hg}}_{\text{O}}.$$
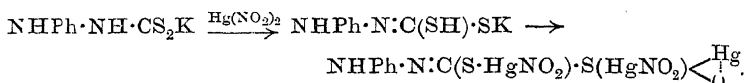
The sulphur atom belonging to the potential mercaptan alone becomes quadrivalent.

Migration of Alkyl Radicles.

When thiocarbanilide methyl ether is treated with mercuric nitrite, the methyl group migrates to the neighbouring nitrogen atom, hydrogen taking its place, thus:

$$\text{NHPh·C(:NPh)·SMe} \xrightarrow{\text{Hg(NO}_2)_2} \text{NMePh·C(:NPh)·SH} \longrightarrow$$
$$\text{NMePh·C(:NPh)·S·HgNO}_2.$$
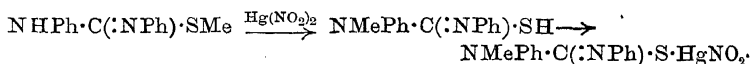
That the reactions described above are of wide application is borne out by the behaviour of 5-methylthiol-2-thio-3-phenyl-2:3-dihydro-1:3:4-thiodiazole, which with mercuric nitrite gives the compound,

$$\begin{matrix} \text{NPh·NMe} \\ | \qquad\quad \\ \text{CS} \underline{\quad\quad} \text{S} \end{matrix}\!\!>\!\text{C(HgNO}_2)·S·HgNO}_2.$$
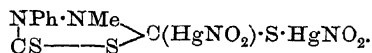
Reaction with the Alkyl Iodides: Formation of Mono-, Di-, and Tri-sulphonium Compounds.

The reaction follows the general course with this material difference, that the complex radicle, being overweighted, can no longer retain its entity, but the less stable part of it is usually ruptured. Of special significance from this point of view is the rupture of the ring of the heterocyclic mercaptide nitrites. When the mercaptide nitrite of 5-thiol-2-thio-3-phenyl-2:3-dihydro-1:3:4-

thiodiazole is digested with an alkyl iodide, the product (I) is obtained, and by further action of the alkyl iodide, the phenyl

$$
\underset{\text{(I.)}}{\overset{\text{HgI \quad R}}{R \cdot NPh \cdot N:CR \cdot \overset{|}{\underset{I}{S}} - \quad \overset{|}{\underset{I}{S}}R}} \qquad
\underset{\text{(II.)}}{\overset{\text{HgI \quad R}}{NR_2 \cdot N:CR \cdot \overset{|}{\underset{I}{S}} - - \overset{|}{S}R}} \qquad
\underset{\text{(III.)}}{\overset{\text{HgI \quad R}}{NR_2 \cdot NR \cdot CR_2 \cdot \overset{|}{\underset{I}{S}} - \quad - \overset{|}{\underset{I}{S}}R}},
$$

group is displaced by the alkyl group and the compound (II) is formed. Finally, two more alkyl groups are attached, with the production of the compound (III).

By the action of methyl iodide, two compounds corresponding with stages (I) and (III) have been isolated, whereas in the case of ethyl iodide only one compound has been obtained, which corresponds with stage (II).

When 2-thio-3-phenyl-2:3-dihydro-1:3:4-thiodiazole disulphide dissolved in carbon disulphide was heated under reflux with ethyl and mercuric iodides, not only was there no rupture of the thiodiazole rings, but one of the tertiary nitrogen atoms became quaternary by combining with a molecule of ethyl iodide, and the following compound,

$$
\overset{\text{HgI \quad Et}}{\underset{\overset{|}{\underset{I}{CS}}---S}{NPh \cdot NEtI}} C \cdot \overset{|}{\underset{I}{S}} --- \overset{|}{\underset{I}{S}} C \overset{N \cdot NPh}{\underset{S--CS}{}},
$$

was obtained.

The action of alkyl iodides on phenyl mercaptide nitrite follows the usual course and yields compounds of the general formula $PhRS_2, HgI_2, RI$.

An interesting monosulphonium compound has been obtained from the mercaptide nitrite of thiocarbanilide. The reaction probably takes place as shown below:

$$
NHPh \cdot C(:NPh) \cdot S(HgNO_2) \overset{Hg}{\underset{I}{<}} \quad {}^{EtI} \quad CEt_2I \cdot SEtI \cdot HgI.
$$

The interaction of mercaptide nitrites of thiocarbanilide alkyl ethers and alkyl iodide takes place as follows:

$$
NRPh \cdot C(:NPh) \cdot S \cdot HgNO_2 \qquad {}^{R'I}
$$

$$
\underset{}{\overset{\text{HgI \quad R'}}{NRPh \cdot C(:NPh) \cdot \overset{|}{S} --- \overset{|}{S} \cdot C(:NPh) \cdot NRPh}} \longrightarrow \overset{\text{HgI \quad R'}}{R' \cdot \overset{|}{S} --- \overset{|}{S} R'} .
$$

*Interaction of the Potassium Salt of 5-Thiol-2-thio-3-phenyl-2:3-
    dihydro-*1:3:4*-thiodiazole and Mercuric Nitrite : Formation
    of the corresponding Mercaptide Nitrite,*

$$\begin{array}{c} \text{NPh·N} \\ | \\ \text{CS----S} \end{array} \!\!\! > \!\! \text{C·SHgNO}_2.$$
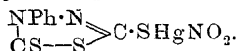
The mercury salt was obtained sometimes anhydrous, but often combined with three, five, or eight molecules of water, the degree of hydration evidently depending on the dilution of the reacting substances. They all evolved nitrous fumes when treated with hydrochloric acid :

0·2724 gave 0·1187 Hg.   Hg = 43·59.

0·1100   ,,   0·0810 CO_2 and 0·0187 H_2O.   C = 20·08; H = 1·89.

0·1420   ,,   10·2 c.c. N_2 at 25° and 760 mm.   N = 8·10.

$C_8H_5O_2N_3S_3Hg$ requires Hg = 42·46 ; C = 20·38 ; H = 1·06 ; N = 8·92
                              per cent.

The above with $3H_2O$:

Found : Hg = 38·05 ; C = 18·28 ; H = 3·29 ; N = 8·30 ; S = 18·56.

Calc. : Hg = 38·09 ; C = 18·29 ; H = 2·1 ; N = 8·00 ; S = 18·29 per cent.

The compound with $5H_2O$:

Found : Hg = 35·75 ; C = 16·92 ; H = 3·20.

Calc. : Hg = 35·65 ; C = 17·12 ; H = 2·67 per cent.

The compound with $8H_2O$:

Found : Hg = 32·10 ; C = 15·10 ; H = 3·56 ; N = 6·16 ; S = 15·08.

Calc. : Hg = 32·52 ; C = 15·63 ; H = 3·41 ; N = 6·83 ; S = 15·61 per cent.

Mercuric Nitrite and Phenyl Mercaptan.

Three different compounds have been isolated in this case. When an alcoholic solution of phenyl mercaptan is added slowly to an excess of mercuric nitrite solution, the reaction takes the ordinary course, and the mercaptide nitrite, $PhS·HgNO_2$, is mainly formed. It is a dull yellow, light granular powder, and is a true nitrite. When, however, the mercaptan is rapidly added in excess, the whole of the mixture assumes a dirty yellow colour and nitrous fumes are evolved.   On keeping, a white, granular powder is obtained which, when crystallised from hot benzene until quite pure, melts sharply at 146°. Under slightly varying conditions, an oxy-compound, $(3PhS,HgO)_2$, is formed. As is evident, it is not easy to control the reaction so as to give one product to the ex-

clusion of the others. The mercaptide nitrite is always found to be admixed with the other products of this reaction.

The mercaptide nitrite gave different results of analysis on different occasions, depending on the proportion of the compound, Ph_2S_3Hg, admixed with it; generally, however, the values were found to be intermediate between those required for the pure material and the compound, Ph_2S_3Hg.

The compound, Ph_2S_3Hg, melting at 146°, gave the following results:

0·1942 gave 0·0864 Hg and 0·3134 $BaSO_4$. Hg = 44·48; S = 22·16.

0·0964 gave 0·116 CO_2 and 0·0230 H_2O. C = 32·17; H = 2·7.

$C_{12}H_{10}S_3Hg$ requires Hg = 44·44; S = 21·30; C = 32·00; H = 2·30 per cent.

The compound, $(3PhS,HgO)_2$, gave the following results:

0·4016 gave 0·1506 Hg. Hg = 37·50.

0·4333 ,, 0·5620 $BaSO_4$. S = 17·82.

0·1230 ,, 0·1886 CO_2. C = 41·81.

$C_{36}H_{30}O_2S_6Hg_2$ requires Hg = 38·02; S = 18·25; C = 41·07 per cent.

The above two compounds were proved to be non-nitrogenous by combustion analysis.

Mercuric Nitrite and 3-*Phenyl*-5-*methyl*-2-*thiohydantoin*:

Formation of the Compound, $\begin{array}{c} CO-NPh \\ | \\ CHMe\cdot N \end{array}\!\!\!>\!\!C\cdot S\cdot HgNO_2, 2H_2O.$

The compound was greenish-grey:

0·1981 gave 0·0954 HgS and 0·1110 $BaSO_4$. Hg = 41·51; S = 7·69.

0·1774 gave 0·1586 CO_2 and 0·0582 H_2O. C = 24·38; H = 3·65.

0·2836 ,, 20·8 c.c. N_2 at 30° and 760 mm. N = 8·10.

$C_{10}H_{13}O_5N_3SHg$ requires Hg = 41·07; S = 6·57; C = 24·64; H = 2·67; N = 8·63 per cent.

Potential Mercaptans.

Mercuric Nitrite and Phenylthiocarbamide: Formation of the

Compound, $NHPh\cdot C(:NH)\cdot S(HgNO_2)\!\!<\!\!\begin{array}{c} Hg \\ O \end{array}.$

This was deep yellow:

0·3512 gave 0·2350 Hg and 0·1227 $BaSO_4$. Hg = 66·9; S = 4·8.

0·2015 ,, 11·4 c.c. N_2 at 26° and 760 mm. N = 6·40.

$C_7H_7O_3N_3SHg_2$ requires Hg = 65·25; S = 5·22; N = 6·85 per cent.

Mercuric Nitrite and s-*Diphenylthiocarbamide : Formation of the Compound,* $NHPh \cdot C(:NPh) \cdot S(HgNO_2) < {}^{Hg}_{O}$.

This was a brownish-yellow, granular powder:

0·3422 gave 0·1970 Hg and 0·1069 $BaSO_4$.   Hg = 57·57; S = 4·64.
0·3970 ,, 0·1141 CO_2 and 0·0244 H_2O.   C = 22·27; H = 1·94.
$C_{13}H_{11}O_3N_3SHg_2$ requires Hg = 58·07; S = 4·64; C = 22·64; H = 1·60
per cent.

The above compound is only rarely formed.   The product gener-ally obtained conforms to the formula

$$Hg[NPh \cdot C(:NPh) \cdot S \cdot HgNO_2]_2 :$$

0·1555 gave 0·0947 HgS and 0·0741 $BaSO_4$.   Hg = 52·51;
S = 6·55.
0·2275 gave 0·1367 HgS and 0·0992 $BaSO_4$.   Hg = 51·80;
S = 5·99.
    $C_{26}H_{20}O_4N_6S_2Hg_3$ requires Hg = 52·43; S = 5·59 per cent.

Mercuric Nitrite and Thiosemicarbazide : Formation of the Compound, $Hg[N(NH_2) \cdot C(:NH) \cdot S \cdot HgNO_2]_2$.

An aqueous solution of the thio-compound was used.   The pro-duct was a dull yellow, granular powder:

0·2715 gave 0·1870 HgS and 0·1362 $BaSO_4$.   Hg = 68·87;
S = 6·89.
0·1032 gave 11·8 c.c. N_2 at 32° and 760 mm.   N = 12·60.
$C_2H_6O_4N_8S_2Hg_3$ requires Hg = 68·96; S = 7·36; N = 12·87 per cent.

Mercuric Nitrite and Diphenylthiosemicarbazide : Formation of the Compound, $Hg[N(NHPh) \cdot C(:NPh) \cdot S \cdot HgNO_2]_2$.

This is an orange-yellow, granular powder:

0·1797 gave 0·0925 Hg.   Hg = 51·48.
0·2577 ,, 0·2498 CO_2 and 0·0523 H_2O.   C = 26·21; H = 2·25.
0·1380 ,, 11·7 c.c. N_2 at 32° and 760 mm.   N = 9·38.
  $C_{26}H_{22}O_4N_8S_2Hg_3$ requires Hg = 51·11; C = 28·57; H = 1·87;
N = 9·54 per cent.

Mercuric Nitrite and Diphenylthiocarbazide : Formation of the Compound, $Hg[N(NHPh)\cdot C(:N\cdot NHPh)\cdot S\cdot HgNO_2]_2$.

This is a pink, granular powder:

0·1667 gave 0·0965 HgS and 0·0607 $BaSO_4$. Hg = 49·91; S = 5·00.

0·1463 gave 0·1404 CO_2 and 0·0327 H_2O. C = 26·14; H = 2·48.

0·1167 ,, 11·7 c.c. N_2 at 30° and 760 mm. N = 11·26.

$C_{26}H_{24}O_4N_{10}S_2Hg_3$ requires Hg = 49·83; S = 5·31; C = 25·91; H = 1·82; N = 11·62 per cent.

Mercuric Nitrite and Phenylhydrazine Phenyldithiocarbazinate : Formation of the Compound,

$$NHPh\cdot N\colon C(SHgNO_2)\cdot S(HgNO_2){<}{\overset{Hg}{\underset{O}{|}}}.$$
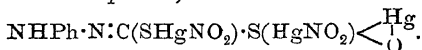
This is a blackish-violet, granular powder:

0·1971 gave 0·1549 HgS and 0·1031 $BaSO_4$.   Hg = 67·71; S = 7·18.

0·1651 gave 8·5 c.c. N_2 at 27° and 760 mm. N = 5·89.

$C_7H_6O_5N_4S_2Hg_3$ requires Hg = 67·40; S = 7·19; N = 6·30; C = 9·44 per cent.

The same compound is formed by the interaction of mercuric nitrite and potassium phenyldithiocarbazinate. (Found: Hg = 67·97; C = 9·24; H = 0·98; N = 5·88 per cent.)

Mercuric Nitrite and Thiocarbanilide Methyl Ether : Formation of the Compound, $NMePh\cdot C(:NPh)\cdot S\cdot HgNO_2$.

This is an orange-yellow, granular powder:

0·2801 gave 0·1038 Hg. Hg = 39·86.

0·2377 ,, 0·3027 CO_2 and 0·0738 H_2O. C = 34·70; H = 3·45.

0·2863 ,, 22·6 c.c. N_2 at 29° and 760 mm. N = 8·99.

$C_{14}H_{13}O_2N_3SHg$ requires Hg = 40·90; C = 34·50; H = 2·67; N = 8·86 per cent.

Mercuric Nitrite and Thiocarbanilide Ethyl Ether : Formation of the Compound, $NEtPh\cdot C(:NPh)\cdot S\cdot HgNO_2$.

The substance is an orange-yellow, granular powder:

0·3730 gave 0·1478 Hg and 0·1874 $BaSO_4$. Hg = 39·63; S = 6·91.

0·1232 ,, 9·4 c.c. N_2 at 32° and 760 mm. N = 8·43.

$C_{15}H_{15}O_2N_3SHg$ requires Hg = 39·92; S = 6·39; N = 8·38 per cent.

Mercuric Nitrite and 5-Methylthiol-2-thio-3-phenyl-2:3-
1:3:4-thiodiazole: Formation of the Compound,

$$\begin{array}{c}\text{NPh·NMe}\\ \text{CS-   --S}\end{array}\!\!>\!\!\text{C(HgNO}_2)\text{·S·HgNO}_2,8\text{H}_2\text{O}.$$
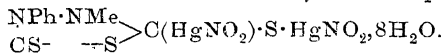
A clear solution of the thio-compound in chloroform was vigorously agitated with mercuric nitrite solution for nearly half an hour, when an emulsion was formed which, after being allowed to remain overnight, gave a cream-coloured, granular mass:

0·1984 gave 0·1055 HgS and 0·1384 BaSO$_4$. Hg = 45·85;
S = 9·58.

0·1879 gave 0·0884 CO$_2$ and 0·0296 H$_2$O. C = 12·83; H = 1·75.

0·1603 ,, 10·2 c.c. N$_2$ at 30° and 760 mm. N = 7·03.

C$_9$H$_{24}$O$_{12}$N$_4$S$_3$Hg$_2$ requires Hg = 45·67; S = 10·96; C = 12·33;
H = 0·91; N = 6·39 per cent.

Mercuric Nitrite and 2-Thio-3-phenyl-2:3-dihydro-1:3:4-thio-
diazole Disulphide: Formation of the Compound,

$$\begin{array}{c}\qquad\qquad\text{Hg—O}\\ \text{NPh·N}\\ \text{CS· --S}\end{array}\!\!>\!\!\text{C·S——S·C}\!\!<\!\!\begin{array}{c}\text{N·NPh}\\ \text{S–CS}\end{array}$$
$$\qquad\qquad\text{NO}_2\quad\text{HgNO}_2$$
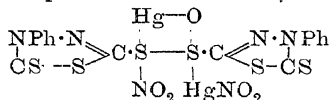
(compare T., 1916, **109**, 133):

0·2940 gave 0·1288 Hg. Hg = 43·80.

0·1190 ,, 9·00 c.c. N$_2$ at 30° and 760 mm. N = 8·35.

C$_{16}$H$_{10}$O$_5$N$_6$S$_6$Hg$_2$ requires Hg = 41·75; N = 8·77 per cent.

Reaction with the Alkyl Iodides.

Interaction of the Mercaptide Nitrite of 5-Thiol-2-thio-3-phenyl-
2:3-dihydro-1:3:4-thiodiazole and Methyl Iodide: Formation
of the Compound,

$$\text{NMe}_2\text{·NMe·CMe}_2\text{·}\overset{\text{HgI}}{\underset{\text{I}}{\text{S}}}\text{——}\overset{\text{Me}}{\underset{\text{I}}{\text{S}}}\text{Me}\;.$$
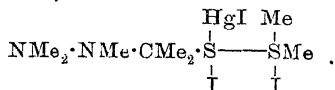
The method of procedure is exactly the same as in the interaction of simple mercury mercaptide nitrites and the alkyl iodides. After heating with methyl iodide under reflux, a portion was left undissolved, which, when purified by washing several times with acetone, melted sharply at 127°. The portion soluble in acetone was purified by precipitation with ether, and melted at 107°:

0·3129 gave 0·0811 Hg. Hg = 25·92.

0·4107 ,, 0·1066 Hg and 0·3718 AgI. Hg = 25·96; I = 48·72.

0·0844 ,, 0·0363 CO_2 and 0·0237 H_2O. C = 11·73; H = 2·45.

$C_8H_{21}N_2I_3S_2Hg$ requires Hg = 25·32; I = 48·23; C = 12·15;
H = 2·66 per cent.

The compound insoluble in acetone has the formula

$$\begin{array}{cc} \text{HgI} & \text{Me} \\ | & | \\ \text{NMePh·N:CMe·S} & \!\!\!\!\!\text{---SMe} \;. \\ | & | \\ \text{I} & \text{I} \end{array}$$
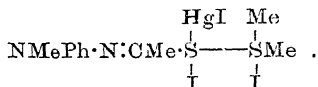
0·1867 gave 0·0449 Hg, 0·1527 AgI, and 0·0870 $BaSO_4$.
Hg = 25·96; I = 48·93; S = 6·40.

0·1070 gave 0·0590 CO_2 and 0·0734 H_2O. C = 15·06; H = 1·39.

0·1227 ,, 4·2 c.c. N_2 at 35° and 760 mm. N = 3·7.

$C_{11}H_{17}N_2I_3S_2Hg$ requires Hg = 24·33; I = 46·35; S = 7·79;
C = 16·06; H = 2·87; N = 3·4 per cent.

Interaction of the above Mercaptide Nitrite and Ethyl Iodide: Formation of the Compound,

$$\begin{array}{cc} \text{HgI} & \text{Et} \\ | & | \\ \text{NEt}_2\text{·N:CEt·S} & \!\!\!\!\!\text{---SEt.} \\ | & | \\ \text{I} & \text{I} \end{array}$$
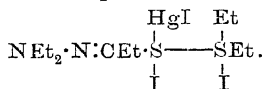
(m. p. 73—74°).

0·2316 gave 0·0572 Hg, 0·1960 AgI, and 0·0972 $BaSO_4$.
Hg = 24·69; I = 45·74; S = 5·77.*

0·2564 gave 0·0611 Hg. Hg = 23·83.

0·1278 ,, 0·0703 CO_2 and 0·0296 H_2O. C = 15·41; H = 2·58.

0·2470 ,, 7·8 c.c. N_2 at 31° and 760 mm. N = 3·50.

$C_{11}H_{25}N_2I_3S_2Hg$ requires Hg = 24·09; I = 45·90; S = 7·72; C = 15·90;
H = 3·07; N = 3·57 per cent.

Phenyl Mercaptide Nitrite and Methyl Iodide: Formation of the Compound, $PhMeS_2,HgI_2,MeI$.

The pure substance was obtained by repeated crystallisation, and was a dull yellow, crystalline powder melting at 90°:

0·4616 gave 0·1252 Hg and 0·4353 AgI. Hg = 27·12; I = 50·96.

0·1131 ,, 0·0551 CO_2. C = 13·29.

$C_8H_{11}I_3S_2Hg$ requires Hg = 26·6; I = 50·66; C = 12·77 per cent.

* See footnote, p. 271.

M*

Phenyl Mercaptide Nitrite and Ethyl Iodide : Formation of the Compound, $PhEtS_2,HgI_2,EtI$ (m. p. 59°).

0·2994 gave 0·0774 Hg and 0·2673 AgI.   Hg = 25·85 ; I = 48·24.
0·1302   ,,   0·0740 CO_2 and 0·0282 H_2O.   C = 15·5 ; H = 1·86.
$C_{10}H_{15}I_3S_2Hg$ requires Hg = 25·64 ; I = 48·84 ; C = 15·39 ; H = 1·92
per cent.

Interaction of the Compound, Ph_2S_3Hg, *and Methyl Iodide : Formation of the Compound*,

$$CH_3 \cdot \overset{I}{\underset{HgI}{S}} \overset{Ph}{\underset{I}{S}} \overset{Ph}{\underset{I}{S}} \cdot CH_3$$
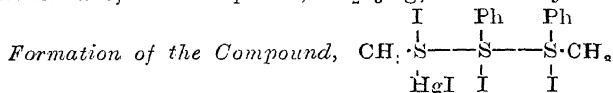
The product was an oil which, on stirring, crystallised.   It was washed several times with acetone, when the colour changed to yellowish-white.   It was insoluble in acetone, and melted at 111—112° :

0·3150 gave 0·0615 Hg, 0·2915 AgI, and 0·2007 $BaSO_4$.   Hg = 19·53 ; I = 50·00 ; S = 8·75.
0·1410 gave 0·0902 CO_2 and 0·0390 H_2O.   C = 17·41 ; H = 3·07.
$C_{14}H_{16}I_4S_3Hg$ requires Hg = 20·24 ; I = 51·42 ; S = 9·71 ; C = 17·00 ; H = 1·62 per cent.

It will be noticed that whenever a sulphonium compound contains phenyl groups, it becomes insoluble in acetone.

Mercaptide Nitrite of Thiocarbanilide and Ethyl Iodide : Formation of the Compound, $CEt_2I \cdot SEtI \cdot HgI$.

In this case, deep purple, needle-shaped crystals were obtained which were soluble in acetone :

0·3083 gave 0·0890 Hg, 0·2920 AgI, and 0·1042 $BaSO_4$.   Hg = 28·73 ; I = 51·18 ; S = 4·64.
· 0·1214 gave 0·0552 CO_2 and 0·0232 H_2O.   C = 12·04 ; H = 2·12.
$C_7H_{15}I_3SHg$ requires Hg = 28·09 ; I = 53·51 ; S = 4·49 ; C = 11·80 ; H = 2·11 per cent.

Mercaptide Nitrite of Thiocarbanilide Methyl Ether and Methyl Iodide : Formation of the Compound, Me_2S_2,HgI_2,MeI.

The mercaptide nitrite was heated under reflux with methyl iodide.   It was obtained pure by fractional precipitation from a

concentrated solution in acetone by adding ether and repeating the process five or six times, when a fairly good crop was obtained which melted at 160—162°:

0·3290 gave 0·0791 Hg and 0·3281 AgI.   Hg=29·51; I=53·89.
0·1150   ,,   0·0221 CO_2 and 0·0218 H_2O.   C=5·24; H=2·11.
$C_3H_9I_3S_2Hg$ requires Hg=28·98; I=55·21; C=5·22; H=1·30

per cent.

Mercaptide Nitrite of Thiocarbanilide Ethyl Ether and Ethyl Iodide: Formation of the Compound, Et_2S_2,HgI_2,EtI.

The procedure was almost the same as in the previous instance. On concentrating the acetone solution, a portion crystallised out, which was purified by repeated fractional crystallisation; when pure, it melted sharply at 111°:

0·3127 gave 0·0862 Hg and 0·0978 AgI.   Hg=27·57; I=51·46.
0·0861   ,,   0·0327 CO_2 and 0·0255 H_2O.   C=10·37; H=3·29.
$C_6H_{15}I_3S_2Hg$ requires Hg=27·32; I=52·05; C=10·37; H=3·29

per cent.

2-Thio-3-phenyl-2 : 3-dihydro-1 : 3 : 4-thiodiazole Disulphide, Mercuric Iodide, and Ethyl Iodide: Formation of the Compound,

$$\underset{\overset{|}{CS}\text{---}\overset{}{S}}{NPh\cdot NEtI}{>}C\text{-}\underset{\overset{|}{I}}{\overset{HgI}{\underset{|}{S}}}\text{---}\underset{\overset{|}{I}}{\overset{Et}{\underset{|}{S}}}\text{-}C{<}\underset{S\text{-}CS}{N\cdot NPh} \quad .$$
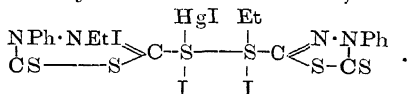
0·3127   gave   0·0512   Hg,   0·2366   AgI,   and   0·3026 $BaSO_4$.
   Hg=16·38; I=40·89; S=13·29.*
0·1574 gave 0·1066 CO_2.   C=18·47.
$C_{20}H_{20}N_4I_4S_6Hg$ requires Hg=16·45; I=41·75; S=15·75; C=19·74

per cent.

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* Owing to the tedious process involved in analysis, the values for sulphur and iodine are sometimes too low (compare T., 1916, **109**, 135).

XXVIII.—*The Reaction between Sodium Chloride Solution and Metallic Magnesium.*

By WILLIAM HUGHES.

COLD aqueous solutions of various salts, including sodium chloride, sodium hydrogen carbonate, sodium carbonate, and magnesium sulphate, were found to react with magnesium powder with considerably more speed than one would expect, since cold water acts very slowly on the metal, and solutions of alkali hydroxides not at all.

That the metal slowly dissolves in solutions of its own salts with the formation of hydrogen, the hydroxide, or a basic salt, has been observed by Kippenberger (*Chem. Zeit.*, 1895, **19**, 269), Vitali (*L'Orosi*, 1895, **18**, 289), Lemoine (*Compt. rend.*, 1899, **129**, 291), Bryant (*Chem. News*, 1899, **79**, 75), Kahlenberg (*J. Amer. Chem. Soc.*, 1903, **25**, 380), and Roberts and Brown (*ibid.*, 1903, **25**, 801).

Liberation of the metal together with hydrogen from various salt solutions by magnesium has been described by Commaille (*Compt. rend.*, 1866, **63**, 556), Clowes and Caven (P., 1897, **13**, 221), Divers (P., 1898, **14**, 57), Tommasi (*Bull. Soc. chim.*, 1899, [iii], **21**, 885), and Faktor (*Pharm. Post*, 1905, **38**, 153).

Lohnstein (*Zeitsch. Elektrochem.*, 1907, **13**, 612) found that the action of magnesium on acetic acid was catalysed positively by the addition of some salts and negatively by others.

Knapp (*Chem. News*, 1912, **105**, 253) found that palladium chloride solutions, and Michailenko and Mushinsky (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 181) that the water of crystallisation of certain salts, were acted on by magnesium with the evolution of hydrogen.

EXPERIMENTAL.

In the preliminary experiments, it was found that 0·329 gram of ordinary magnesium powder and 35·3 c.c. of 2N-sodium chloride solution gave 291·4 c.c. of a gas at the end of a week. The metal darkened, and a white, gelatinous solid was disseminated throughout the liquid. The greyish-black powder slowly changed to a compact, white solid, but the reaction was not quite complete at the end of seven days. The theoretical yield of hydrogen is 325 c.c. at $N.T.P.$

One c.c. of the original sodium chloride solution and 1 c.c. of the solution which had been acted on by the magnesium gave a

titre of 13·62 c.c. and 13·70 c.c. respectively with silver nitrate. 38·6 C.c. of the gas after absorption for fifteen minutes over freshly prepared alkaline pyrogallol measured 37·5 c.c.

These results were taken to indicate that the gas was hydrogen only, and it was determined to seek a relation, if any, between the rate of evolution of gas and the concentration of the sodium chloride solution.

The method adopted was to add known amounts of magnesium to the different solutions which had been saturated with hydrogen, and to measure the initial velocity of the reaction by reading the volume of hydrogen evolved at 25°, without shaking, at short intervals for a total period of two or three minutes.

Magnesium.—A supply of ordinary magnesium powder, apparently quite bright and free from oxide, was fractionally sifted, and the portion passing through between sieves of 90 and 60 meshes to the inch, respectively, was used. (0·0692 gave 0·3075 $Mg_2P_2O_7$; by Gibbs's method, $Mg = 97·03$. 0·0258 gave 25·4 c.c. H_2 [dry at 16·5° and 726 mm.] $Mg = 96·45$ per cent.) Only traces of aluminium and zinc could be detected in the substance. Since the phenomena investigated seemed to depend on the nature of the solutions and not on the small amounts of impurity in the magnesium, it was considered unnecessary to attempt any purification of this reagent.

Sodium Chloride.—Common salt was dissolved in distilled water, filtered, and the solution rendered just alkaline with sodium hydroxide and filtered again. The slightly alkaline solution was evaporated with continual stirring, and the first crop of crystals were well drained and kept over concentrated sulphuric acid.

Water.—Distilled water was redistilled in a glass still which had been previously well steamed out. This water was boiled under diminished pressure previous to being used.

Hydrogen.—This was prepared from zinc and pure sulphuric acid, and purified by passing through lead nitrate solution, silver nitrate solution, a soda-lime tower, and then a set of sodium hydroxide bulbs, and stored over water.

Solutions.—These were made up by weight. The number of molecules of water to each molecule of sodium chloride is represented by c.

Apparatus.—At first the solution—10 cm. deep—was contained in a test-tube, and the hydrogen measured in a nitrometer, the volume being read every fifteen minutes.

The rate was constant in each case for about five hours. The

initial rate was read from the tangent to the curve, and reduced to c.c. at $N.T.P.$ per gram of magnesium per hour.

In the second case, a conical flask was chosen as reaction vessel in order to have a smaller hydrostatic pressure on the magnesium. It was fitted with a rubber stopper carrying a delivery tube, A (Fig. 1), drawn to a point at the bottom of the flask, for the entry of hydrogen, an exit tube, B, which could be closed, and a water manometer, C, behind which was fixed a millimetre scale.   Selected

FIG. 1.
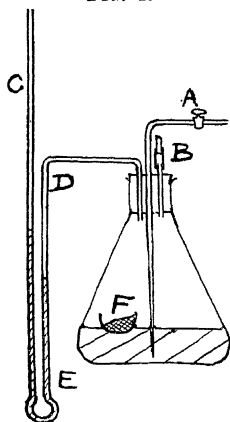
quill tubing was used in making it, and it was carefully calibrated with distilled water at 25°, and found to be of uniform bore for the part calibrated, namely, the length DE. 1 cm. $= 0.1880$ c.c. at 25°.   Twice distilled water saturated with hydrogen was used in the manometer.   The weighed magnesium was floated on a capsule on the solution, the volume of which was always 25 c.c., and then the air displaced by, and the solution saturated with, hydrogen through A and B for not less than ten minutes, all being immersed in the bath.   The apparatus was quickly shaken, and simultaneously a stop-watch was started.   The volumes of hydrogen read off every half- or quarter-minute were reduced to $N.T.P.$, tabulated (table I), and plotted (Fig. 2, curves 1 and 2).   The initial

rate was obtained by drawing the tangent as shown.   The kind of induction period at the start is much more pronounced with the more concentrated solutions, and is probably due to surface-tension effects, chiefly in the manometer.

TABLE I.

$= 30.$

$\frac{1}{4}$ minute intervals.	Manometer, Δ (in cm.).	Hydrogen, c.c.	Total pressure (corr.).	Hydrogen c.c. corrected.
0	0·6	0	—	0
1	0·9	0·15	753·9	0·0256
2	1·7	0·55	754·4	0·0941
3	2·3	0·85	754·9	0·1454
4	2·9	1·15	755·3	0·1969
5	3·4	1·40	755·7	0·2397
6	3·8	1·60	756·0	0·2742
7	4·2	1·80	756·3	0·3086
8	4·5	1·95	756·5	0·3344
9	4·8	2·10	756·7	0·3601
10	5·1	2·25	756·9	0·3860

TABLE I. (*continued*).

$c = 38$.

¼ minute intervals.	Manometer, Δ (in cm.).	Hydrogen, c.c.	Total pressure (corr.).	Hydrogen, c.c. corrected.
	0·36	0	—	0
	0·78	0·21	754·0	0·0359
	1·40	0·52	754·4	0·0889
	1·98	0·81	754·9	0·1387
	2·48	1·06	755·2	0·1814

FIG. 2.
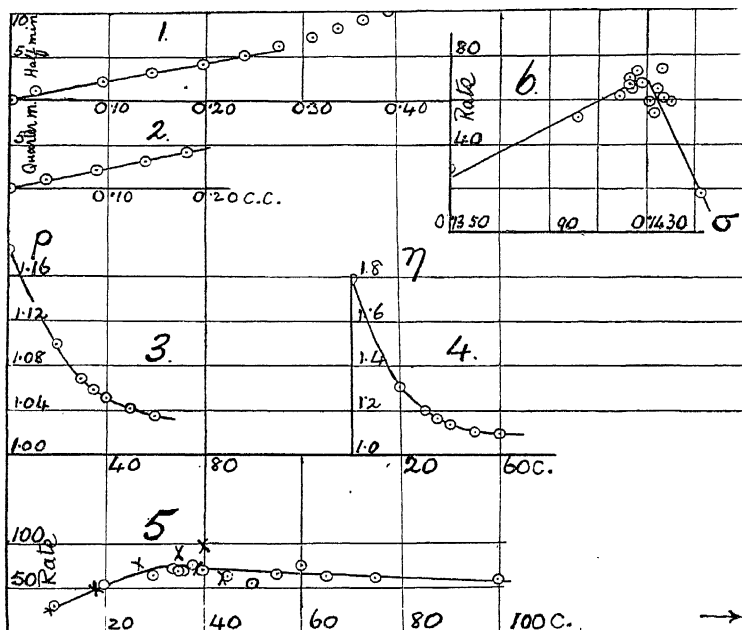
The greatest precautions were taken that the solutions of sodium chloride were in each case quite free from acid. Immediately at the end of a determination they reacted alkaline.

The viscosities were determined with an Ostwald viscosimeter, the essential precautions being observed (Applebey, T., 1910, **97**, 2000; from the equation

$$\eta = \eta_{\text{water}} \times \frac{\text{density of solution}}{\text{density of water}} \times \frac{\text{time of flow of solution}}{\text{time of flow of water}}.$$

The densities were determined with a pyknometer, the weighings being carried out with a similarly treated counterpoise. These were as shown in table II. The curves are plotted in Fig. 2, 3 and 4.

TABLE II.

Concentration.	$\rho_{4°}^{27°}$.	$\eta_{25°}$.
10	1·184	1·794
20	1·099	1·303
30	1·068	1·198
35	1·058	1·165
40	1·051	1·134
50	1·041	1·101
60	1·034	1·095

In table III are given the initial rates for the different concentrations of sodium chloride solutions.

TABLE III.

Time, hrs. min.	Tempera- ture.	Pressure, mm. (corr.)	Vol., c.c. (corr.)	c.	nesium, Gram.	Rate.	Remarks.
13 30	19°	762·3	31·32		0·0984	23·5	First method.
2 20	20	763·9	11·99	18	0·1069	48·1	
15	22	766·5	1·87	27	0·0995	75·1	
1 20	25	758·7	8·32	45	0·1004	62·2	
16	24	758·3	2·29	35	0·0985	87·3	
15	22·5	766·1	2·42	·40	0·1004	96·5	
15	23	767·1	1·58	44	0·1018	62·2	
16	23	768·3	1·87	39	0·0977	71·6	
4	25	749·5	0·72	30	0·1165	93·1	
7	25	749·8	0·18	30	0·0333	46·6	
3	24·1	749·9	0·45	30	0·1798	50·4	Method not accurate enough.
2	19·2	749·2	0·51	30	0·1513	100·5	
1·5	20	749·2	0·37	30	0·1184	124·1	
0·5	25	749·4	0·0425	30	0·0840	60·7	
		749·4	0·0710	30	0·1367	64·3	Second method. Better agreement.
		750·5	0·0683	30	0·1248	62·3	
		752·8	0·03845	10	0·1590	29·0	
		752·9	0·0664	20	0·1531	52·1	
		753·2	0·0479	30	0·1062	54·2	
		754·8	0·0944	35	0·1702	66·6	
0·25		752·9	0·0684	40	0·1216	67·5	
		752·3	0·0342	50	0·1507	54·4	Quarter minute intervals.
0·5		757·0	0·0417	60	0·1343	74·6	
		753·4	0·0135	32	0·0955	17·0	Metal wetted accidentally during bubbling in hydrogen.
0·25		753·4	0·0513	34	0·1767	69·7	
		753·4	0·0531	36	0·1940	65·7	
		753·4	0·0454	38	0·1478	73·6	
		754·8	0·0343	45	0·1412	59·5	
		754·8	0·0411	55	0·1518	65·0	
		754·8	0·0411	65	0·1581	62·4	
		754·7	0·0386	75	0·1502	61·6	
		755·2	0·0429	100	0·1722	59·7	
		750·6	0·0148		0·1969	18·0	Water only

These rates are plotted against concentrations in curve 5. The arrow indicates the rate for water ($c = \infty$), and the crosses denote the values obtained with the nitrometer.

Results.

No great accuracy can be claimed for the numerical values, chiefly because the assumption that the total area of equal weights of the sifted magnesium is constant is only approximately true. However, it is evident that curve 5 passes through a maximum at $c = 32$; also the surface density of water molecules in contact with magnesium (neglecting surface concentration effects) is given by $\{c\rho/(cM_w + M_s)\}^{\frac{2}{3}}$, where M_w is the molar weight of water, M_s that of sodium chloride, and ρ the density of the solution. Values of this expression ($= \sigma$) have been found for various concentrations and then plotted against the corresponding rates in curve 6. This passes through a maximum for $\sigma = 0.1426$ about, or $c = 37$. One would expect a maximum rate for $c = \infty$ — pure water, since then the magnesium surface would be apparently open to attack by a denser population of water molecules. Again, the values of the viscosity, hydrostatic pressure, and surface tension (Forch, *Ann. Physik*, 1905, [iv], **17**, 744) are each greater for $c = 32$ than for weaker solutions, so it seems that the maximum at $c = 32$ is not due to any special ease of expulsion of gas through the solution. Further, the specific conductivity of sodium chloride solutions steadily increases to a maximum at the saturation point, so that at $c = 32$ the conductivity is not best suited for electrolytic action of impurities in the magnesium to take place.

Conclusions.

(1) Both alkaline and neutral salts positively catalyse the reaction between ordinary magnesium and purified water at the ordinary temperature.

(2) With sodium chloride solutions, the rate of evolution of hydrogen depends on the concentration, the differences being easily detected by the eye. The initial rates for approximately equal areas of magnesium in contact with different concentrations of sodium chloride solutions have been measured, and a maximum has been found for a solution of 32 molecules of water per molecule of sodium chloride.

(3) It is considered that the existence of this maximum points to a specific effect of the dissolved sodium chloride on the water.

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XXIX.—*The Theory of Duplex Affinity.*

By Samuel Henry Clifford Briggs.

In a former paper (T., 1908, **93**, 1564) it was shown how the old conception of duplex affinity can be applied in devising constitutional formulæ for complex inorganic compounds. In a subsequent paper (*ibid.*, 1917, **111**, 253), the theory of duplex affinity was treated from the point of view of the electrical structure of matter. It was assumed that every element is able to exert both positive and negative affinity, positive affinity being a tendency to lose electrons and negative affinity a tendency to attract electrons. A further distinction was made between primary and secondary affinity, the secondary affinity being opposite in sign to the primary affinity, and only coming into action after the primary affinity has been satisfied. By means of these assumptions, it was possible to correlate a number of apparently disconnected phenomena, including the structure and stability of complex compounds, the strength of acids and bases, polymerisation, etc.

The present communication is concerned more particularly with secondary affinity, and some conclusions have been reached which have made it possible to apply the theory of duplex affinity in several new directions.

Secondary Negative Affinity and Secondary Positive Affinity.

As in the previous paper (T., 1917, **111**, 253), Lodge's view (*Nature*, 1904, **70**, 176) that the electrons in an atom are bound to the positive charge, not by a single line of attraction or elastic thread, but by a bundle of a very large number of lines of force, is adopted. For the sake of simplicity, it is supposed that the atoms are spheres, although this is not an essential feature of the general argument. The volumes of the atomic spheres · are assumed to be directly proportional to the so-called atomic volumes of the elements.

The term "valency" is used in this paper in a strictly electrochemical sense, in accordance with Sir J. J. Thomson's theory (*Phil. Mag.*, 1914, [vi], **27**, 757).

Consider the case of two univalent atoms A and B, which combine to form a compound AB as the result of the transfer of an electron from A to B, A having positive primary affinity and B having negative primary affinity. Owing to the attraction of B for the electron, a number of lines of force which united the

electron to the positive nucleus of the atom A are broken. Call this number u. Then in the atom B, u lines of force joining electrons in the atom B (previous to its combination with A) to its positive nucleus will be loosened, as a result of the passage of the electron from A to B. Suppose, now, that the compound AB undergoes electrolytic dissociation in solution into the ions $A^{\cdot}$ and $B^{/}$. The positive nucleus of the cation $A^{\cdot}$ will be able to bind u lines of force from electrons in other atoms, that is to say, the cation $A^{\cdot}$ will have negative affinity, and in this way the secondary negative affinity of the element A arises. The electrons in the anion $B^{/}$, on the other hand, will have u lines of force loosened, and therefore be able to attach themselves to the positive nuclei of other atoms. Consequently, the anion $B^{/}$ has positive affinity, which is the secondary positive affinity of the element B.

Attention must now be directed to a fundamental difference between secondary negative affinity and secondary positive affinity. According to the modern views on the electrical structure of matter, the positive nucleus is situated at the centre of the atom, and its spatial dimensions are extremely minute compared with the volume of the atom as a whole. As we have seen above, however, secondary negative affinity arises from the power of the nucleus to attract lines of force (or electrons). Since the nucleus is at the centre and is so exceedingly small, it follows, so far as the effect on other atoms is concerned, that secondary negative affinity may be regarded as an attractive force distributed equally over the surface of the atomic sphere.

Secondary positive affinity, on the other hand, emanates from the outer electrons (valency electrons or mobile corpuscles) in the atom. The secondary positive affinity cannot therefore be regarded as being equally distributed over the atomic sphere, but must be confined to certain individual electrons or rings of electrons. In other words, secondary negative affinity conforms to Werner's theory of affinity ("Neuere Anschauungen auf dem Gebiete der anorganischen Chemie," 3rd ed., p. 83), whereas secondary positive affinity does not. This difference between secondary negative affinity and secondary positive affinity appears to be of considerable importance in the building up of inorganic compounds, as will be more clearly seen below.

When the ions $A^{\cdot}$ and $B^{/}$ combine to form the molecule AB, some of the loosened lines of force in B will be attached to the positive nucleus of A, as shown by the "ionic formula" $\cdots\rightarrow A^{\cdot}\leftarrow B^{/}\cdots\rightarrow$ (T., 1917, 111, 253). If the number of lines of force thus attached is denoted by v, then in the compound AB the positive nucleus of A is still able to bind $u-v$ lines of force,

whereas the electrons in B have still $u-v$ lines of force loosened and capable of attachment to the nuclei of other atoms. The number $u-v$, therefore, represents the unsaturated secondary negative affinity of A and the unsaturated secondary positive affinity of B, indicated by the dotted arrows in the "atomic formula" ----A⟶B---- and in the "ionic formula" ----$A^{\cdot}$---B'---- (T., 1917, **111**, 253).*

Influence of Atomic Volume.

Since the secondary negative affinity is distributed equally over the surface of the atomic sphere, it follows that when the atomic volume is large, v will be correspondingly small and $u-v$ proportionately large (see p. 286). When the compound AB is dissolved in a dissociating medium, such as water, the molecules of the solvent combine with A and B by means of the unsaturated secondary affinity, thereby bringing about dissociation into the ions $A^{\cdot}$ and B' (compare T., 1908, **93**, 1564). Therefore, if $u-v$ is large, AB will be a strong electrolyte. As shown above, however, $u-v$ is large when the atomic volume of A is large, and this is the reason why the salts of the alkali metals are the strongest electrolytes.

On the other hand, although when the atomic volume of A is large the total unsaturated affinity is correspondingly large, nevertheless the *intensity* of the affinity per unit area of the atomic sphere varies *inversely* as the square of the radius, and is therefore large when the atomic volume of A is small. Consequently, the molecular compounds $(nM \cdot A)B$, formed by satisfying the free secondary negative affinity of A by the free secondary positive affinity of n molecules of a compound M (such as ammonia or water) (T., 1917, **111**, 253), will be most clearly defined and stable

---

* Three types of combination are distinguished: (1) Combination due to primary affinity only, as in the formula ----⟶ A ⟶ B ----⟶, the passage of the electron from A to B being indicated by the thick arrow pointing from A to B. (2) Combination due to secondary affinity only as seen in molecular compounds, such as $2H_3N$ ⟶ CuCl, the union of the electrons in the nitrogen atom to the positive nucleus of the copper atom being indicated by the thin arrow pointing from nitrogen to copper. (3) Combination due to both primary and secondary affinity as in the non-polar compound $A \rightleftharpoons B$.

It should be noted that the formulæ ----⟶ A ⟶ B ----⟶ and $A \rightleftharpoons B$ represent the limiting cases of the strongest possible electrolyte and the truly non-polar compound respectively. Most compounds will come in between the two formulæ. A compound of intermediate properties might therefore be written ----⟶ $A \rightleftharpoons B$----⟶, but it is often convenient to write it as a compound of charged ions rather than of atoms, and in this way the "ionic formula" ----⟶ $A^{\cdot}$ ⟵ B' ⟶ is derived.

when the volume of A is small.   As a matter of fact, those elements which form the most stable complex compounds are all found in the depressions of the atomic volume curve (chromium, manganese, iron, cobalt, nickel, copper, zinc, ruthenium, palladium, rhodium, silver, osmium, platinum, iridium, and gold) (see also the work of Ephraim on the effect of the atomic volume of the central atom on the stability of metal–ammonia compounds, *Ber.*, 1912, **45**, 1322).

Conversely, the same reasoning elucidates the somewhat contradictory phenomenon that many of the salts of the alkali metals which are readily soluble in water separate from solution in the anhydrous state.   These salts dissolve readily, because of the large value of $u–v$.   They do not give stable hydrates, because of the small intensity of the affinity per unit area of the atomic sphere which results from the large atomic volume of the alkali metals.

Non-polar Compounds.

If the two ions $A^{\cdot}$ and $B^{\prime}$ were to combine in such a way that the secondary affinities completely saturated each other, then the electron would be pulled back into A and the atoms would be held in combination by means of two equal bundles of lines of force, one passing from the nucleus of A to the electrons of B, and the other from the nucleus of B to the electrons in A.   That is to say, AB would be a non-polar compound, as shown by the formula $A \rightleftharpoons B$.

The conception of secondary negative affinity developed above (p. 279) leads to the following conclusions with regard to the conditions for the formation of non-polar compounds in those cases in which the valency of the element A with primary positive affinity is fully saturated.   The conclusions do not, however, apply when A is not exerting its full valency, as the mobile corpuscles still remaining on A introduce complications.

The compounds to be considered, therefore, are those represented by the formula AB_x, in which x varies from 1 to 8 when B is a univalent atom.

When $x = 1$, the secondary negative affinity of A is only partly saturated, as already explained (p. 280), because only a part of the spherical surface of A comes under the influence of B.   If $x = 2$, and A is therefore united to two atoms of B, a larger part of the spherical surface of A is affected, and in general as x increases, more and more of the spherical surface of A is brought under the influence of B.   Hence as x increases, the tendency of AB_x to undergo electrolytic dissociation decreases (see p. 280).

The salts of the metals in the earlier groups of the periodic table are therefore the strongest electrolytes, and the electrolytic properties become less marked in the compounds of the metals with higher valency (when they are exerting their full valency).

If, however, AB_x is to be a truly non-polar compound, the secondary negative affinity of A, which is distributed equally over the surface of the atomic sphere, must be completely saturated, and the optimum condition for such complete saturation will be reached when the atoms of B are symmetrically distributed in space around the spherical surface of A.

Since the maximum valency is 8, the number of cases of symmetrical distribution is strictly limited. If B is univalent, x may be 4, 6, or 8, when the atoms of B will be distributed around the spherical surface of A at the corners of a regular tetrahedron, a regular octahedron, and a cube respectively. If B is bivalent, the only possible case is $x = 4$, when the B atoms are situated at the corners of a regular tetrahedron. We should therefore expect to find the non-polar properties most strongly marked in compounds having the formulæ AB_4, AB_6, and AB_8 when B is univalent, and AB_4 when B is bivalent.

Since the forces between the molecules of non-polar compounds are small (Thomson, *loc. cit.*, p. 760), such compounds, in addition to their inability to undergo electrolytic dissociation, will also be comparatively volatile and more or less inert. There are several striking instances of compounds with these characteristics in the four classes of substances under discussion.

In the group AB_4 we have the typically non-polar compounds, methane and carbon tetrachloride.

The formula AB_6 is represented by the gaseous sulphur hexafluoride, SF_6, which is almost as inert as nitrogen (Moissan and Lebeau, *Compt. rend.*, 1900, **130**, 865, 984; Berthelot, *Ann. Chim. Phys.*, 1900, [vii], **21**, 205), and by the gaseous tungsten hexafluoride (Ruff and Eisner, *Ber.*, 1905, **38**, 742), WF_6.

Only one compound of the formula AB_8 has hitherto been prepared. This is osmium octafluoride (Ruff and Tschirsch, *Ber.*, 1913, **46**, 929), which boils below 50°, and is a highly stable although reactive substance.

The class AB_4, in which B is bivalent, includes the remarkable tetroxides of ruthenium and osmium, RuO_4 and OsO_4. These compounds both boil at about 100°, and are so completely saturated that they are incapable of combination with alkali hydroxides. Indeed, osmium tetroxide can be distilled off from its solution to which an alkali has been added (compare Ostwald, "The Principles of Inorganic Chemistry," p. 757).

Although symmetry of structure is thus often associated with, and conduces to, non-polarity, it does not follow that all symmetrical compounds will be without polarity, as other factors, such as the relative atomic volumes of A and B, will also exert an influence.

Conversely, when A is *not* exerting its full valency, non-polar combination is possible in substances which are not spatially symmetrical. Thus, according to Thomson (*loc. cit.*), carbon monoxide and nitrous oxide are non-polar compounds.

Other examples given by Thomson bring out the relationship between symmetry and non-polarity in another way. Although both carbon tetrachloride, CCl_4, and methane, CH_4, are truly non-polar, nevertheless chloroform, $CHCl_3$, and methyl chloride, CH_3Cl, are polar compounds.

Werner's Co-ordination Numbers and the Co-ordination Formula.

Suppose the cation $A^{\cdot}$ combines with n molecules of a compound M possessing free secondary positive affinity, such as ammonia or water, to give the complex ion $(nM . A)^{\cdot}$. Here also the conditions for maximum saturation of the secondary negative affinity of A will involve spatial symmetry in precisely the same way as was seen to apply in the formation of non-polar compounds. The maximum value of n should therefore be either 4, 6, or 8, according to the relative volumes of the atom A and the molecule M; but the maximum value of n is the maximum co-ordination number of the element A, and Werner (*loc. cit.*, p. 52) has shown that this is either 4, 6, or 8. It would appear, also, that the geometrical relationship existing between the volumes of the central atom A and the molecule M is of more importance than the intensity of the affinity in determining the value of the co-ordination number. We find, for example, that barium, with a comparatively large atomic volume, has the maximum co-ordination number 8, as seen in the compound, $(Ba8NH_3)Cl_2$, whereas cobalt, with a much smaller atomic volume, has the maximum co-ordination number 6 in the compound $(Co6NH_3)Cl_3$, in spite of the fact that cobaltic salts have a much greater tendency to combine with ammonia than is shown by barium salts. Similarly, boron, with a very small atomic volume, has the maximum co-ordination number 4 in the compound $(BF_4)H$.

Attention must now be directed to the limiting case in which the secondary negative affinity of A is *completely* saturated by the free positive affinity of M, giving the complex ion $(nM . A)^{\cdot}$. In what way will the anion B' combine with this complex cation to

give the molecule $(nM \,.\, A)B$? In discussing this question, we may suppose that M is a molecule of ammonia. In the former papers (T., 1908, **93**, 1564; 1917, **111**, 253), ammonia was written

$$--\mathrm{N}\overset{=\!=\mathrm{H}}{\underset{=\!=\mathrm{H}}{=\!=\mathrm{H}}} .$$
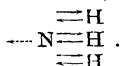
This formula was derived from the facts (1) that the hydrogen atoms do not undergo electrolytic dissociation in solution in water, and therefore have both primary and secondary affinity saturated, and (2) that the nitrogen atom has free secondary positive affinity, as shown by the ease with which ammonia molecules can combine with the free secondary negative affinity of metals in their salts to give metal–ammonia compounds. From the reasoning developed above, however (p. 280), it is clear that this formula for ammonia, although correct so far as it goes, is not quite complete, because if the nitrogen atom still has $u-v$ lines of force loosened, as expressed by the dotted arrow, then each hydrogen atom must be able to bind $u-v$ lines of force to its nucleus. In other words, each

hydrogen atom has still a little free secondary negative affinity. Since, however, the free secondary positive affinity in the ammonia molecule is confined to one atom only (the nitrogen atom), it masks the free secondary negative affinity which is distributed over the three hydrogen atoms. In the general case of a compound $A_m B_n$, in which A and B have free secondary affinity, if m is greater than n the molecule $A_m B_n$ will react as if it had the free secondary affinity of B only. This characteristic will be the more strongly marked the greater the difference between m and n, and it will be all the more intensified the greater the volume of A (the atom with primary positive affinity), and vice versâ. Thus we find that ammonia, water, and potassium chloride react as if they had free secondary positive affinity only in forming complex compounds, whereas cupric chloride, ferric chloride, etc., behave liike substances with free secondary negative affinity.

The complete formula for ammonia should therefore be written

$$--\mathrm{N}\overset{=\!=\mathrm{H}\!\leftarrow\!--}{\underset{=\!=\mathrm{H}\!\leftarrow\,\cdot\cdot}{=\!=\mathrm{H}\!\leftarrow\!--}}$$
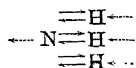
in which each hydrogen atom has a little free secondary negative affinity. Returning now to the combination of the complex $(nM \,.\, A)^{\cdot}$ with the anion B' to give the salt $(nM \,.\, A)B$, we may take the concrete case in which the complex is $(Co6NH_3)^{\cdots}$ and the anion is Cl', and assume that the secondary negative affinity of the cobalt atom is *completely* saturated by the free secondary positive affinity of the nitrogen in the six molecules of ammonia.

The only possible way in which the chloride ions can unite with the complex to give the salt $(Co6NH_3)Cl_3$ is by the saturation of the free secondary negative affinity of the eighteen hydrogen atoms by the positive affinity of the chlorine ions. This gives Werner's co-ordination formula $(Co6NH_3)Cl_3$ exactly, in which, according to Werner's phraseology, the chlorine atoms are united to the outer sphere of the complex.

It should be carefully noted, however, that the co-ordination formula only applies to the *limiting* case in which the secondary negative affinity of A is *completely* saturated by nM in the complex $(nM . A)^{.}$. If this saturation is not complete, then the positive nucleus of A will exert an attraction on the electrons in B, as shown by the "ionic formula" $nM{\rightarrow}A^{.}{-}B'{-}{-}{-}$ (T., 1917, **111**, 260). A familiar example is seen in aquopentammine cobaltic chloride, $\left(Co\dfrac{5NH_3}{H_2O}\right)Cl_3$, which changes spontaneously into chloropentammine cobaltic chloride, $\left(Co\dfrac{5NH_3}{Cl}\right)Cl_2$. Unless the cobalt atom exerts a direct attraction on the chlorine atoms, as shown by the formula $\dfrac{5NH_3{\rightarrow}}{H_2O{-}-}Co^{...}{-}Cl_2'''{-}{\rightarrow}$, it is impossible to understand this spontaneous change.

Application of the Theory of Duplex Affinity to Oxygen Compounds.

In the former papers (*loc. cit.*), most of the examples considered were halogen compounds. The development of the theory of secondary negative affinity in the present communication has made it possible to study oxygen compounds from the point of view of duplex affinity in such a way as to bring out some general relationships which are not touched on by other theories of affinity and valency.

Take the case of a metal, M, which forms a series of oxides, MO, MO_2, MO_3, MO_4. In the oxide MO, in which the oxygen atom has received two electrons from the atom M, only part of the atomic sphere of M will come under the influence of the oxygen atom. Hence the secondary affinity of both atoms will be partly unsaturated, and the formula will be

$$-{-}M\overset{2}{\rightleftharpoons}O\overset{*}{\rightarrow}\cdot$$
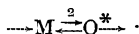
* Instead of denoting the passage of two electrons by two thick arrows $M \rightleftharpoons O$, it is more convenient to write one arrow only, with a small figure above to express the number of electrons which it represents, for example, $M \overset{2}{\rightarrow} O$.

When MO is oxidised to give MO_2, a greater part of the spherical surface of M will come under the influence of the oxygen atoms, and the saturation of the secondary affinity will be more complete than in the first oxide, MO. This will apply still more in MO_3, and most of all in MO_4, in which the oxygen atoms are distributed symmetrically in space around M. In MO_4 we therefore have the possibility of complete saturation of the secondary affinity with the production of a non-polar compound. The oxides OsO_4 and RuO_4, referred to above (p. 282), appear to approximate closely to this condition. The four oxides should therefore be written (assuming that MO_4 is non-polar):

$$\cdots M \overset{2}{=\!\!=} O \cdots \quad \cdots M \overset{4}{=\!\!=} O_2 \cdots \quad \cdots M \overset{6}{=\!\!=} O_3 \cdots \quad M \overset{8}{=\!\!=} O_4.$$
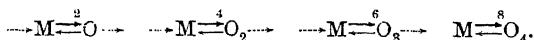
It may perhaps be better to write the non-polar oxide $M \rightleftharpoons O_4$ rather than $M \overset{8}{=\!\!=} O_4$, as the electrons will not have left the M atom in this case.

It should be carefully noted that, since the secondary affinity of M is increased by each addition of an oxygen atom, the saturation of the secondary affinity of the first oxygen atom becomes more complete as oxidation proceeds, because, the secondary affinity of M being distributed equally over the surface of the atomic sphere, the intensity of the affinity present on that part of the spherical surface which comes under the influence of the first oxygen atom will increase with increase in the number of oxygen atoms combined. The *free* secondary affinity of the first oxygen atom will therefore decrease with increasing oxidation of M until in the final, non-polar stage the secondary affinity of the first oxygen atom will be completely saturated. The same reasoning applies, of course, to all the other oxygen atoms as well.

The Hydration of Oxides.—When potassium oxide and water are brought together, there are two ways in which combination may occur. The strongly marked, free secondary positive affinity of the oxygen atom in the potassium oxide may attract the hydrogen atoms of the water, which have slight, unsaturated secondary negative affinity, *or* the unsaturated secondary negative affinity of the potassium may combine with the slight, free secondary positive affinity of the oxygen atom in the water molecule. We may therefore obtain

$$\cdots K_2O \longrightarrow H_2O \cdots \quad \text{or} \quad \cdots H_2O \longrightarrow K_2O \cdots$$
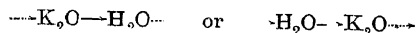
or perhaps a ring structure $K_2 \overset{O \longrightarrow H}{\underset{O \longleftarrow H}{}} $. In potassium, u–v is large, owing to the large atomic volume of potassium (see p. 280), and therefore the unsaturated secondary affinities of the potassium

atoms and the oxygen atoms are large. In water, on the other hand, $u-v$ is small (as seen from the very slight extent to which it is dissociated into hydrogen and hydroxyl ions); hence the unsaturated secondary affinities of the hydrogen atoms and the oxygen atom are small. In each of the three formulæ for K_2O, H_2O, we consequently have the two potassium atoms electrically equal, the two hydrogen atoms electrically equivalent, but the two oxygen atoms very different from each other. The tendency will be for the affinities to be redistributed in such a way as to make the two oxygen atoms also electrically equal, and we therefore have the change $K_2O, H_2O \Longrightarrow 2KOH$. Similar considerations will apply to the hydration of other oxides.

Bases and Acids.—When an oxide is hydrated, the product may be either a base or an acid, according to the manner in which it undergoes electrolytic dissociation in solution. If MOH were a base of the strongest possible type, the formula would be written as (I), and if it were the strongest possible type of acid, as (II) (T., 1917, **111**, 253).

$$\cdot M \longrightarrow O \rightleftharpoons H \qquad\qquad M \rightleftharpoons O \longleftarrow H \cdot$$
$$(I.) \qquad\qquad\qquad (II.)$$
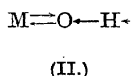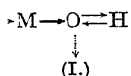
It has already been shown (p. 286) that increase in the number of oxygen atoms implies a more complete saturation of the secondary affinity of all the oxygen atoms already present in the oxide (anhydrous or hydrated). As the secondary affinity of the oxygen atom of the hydroxyl group becomes more completely saturated by the secondary affinity of M, there is less affinity left to saturate the secondary affinity of the hydrogen of the hydroxyl group, and the free secondary affinity of the hydrogen therefore increases. Consequently, the tendency of the hydrogen atom to be electrolytically dissociated becomes greater, and the structure of the hydroxyl group changes from $\longrightarrow O \rightleftharpoons H$ (basic) to $\rightleftharpoons O \longleftarrow H \longleftarrow$ (acidic), with increase in the number of oxygen atoms united to the element M. We therefore have the following general rule:

When a series of oxides of the same element M are hydrated, the hydrate of the highest oxide is the strongest acid (or weakest base). In other words, in a series $M^{OH}_{O_x}$ the greater the value of x the stronger the acidic properties (or the weaker the basic properties).

This rule appears to hold good throughout the periodic table. It is exemplified most clearly in the compounds of the elements in the sixth, seventh, and eighth groups, these being the elements which exhibit the most numerous stages of oxidation. Thus ferrous oxide is basic, ferric oxide less basic (as shown by the greater ease with which ferric salts are hydrolysed), and iron trioxide is acidic. The oxides of chromium form a similar series from the basic chromous and chromic oxides to the acidic chromium trioxide. Manganous oxide is basic, manganic oxide less basic, and manganese dioxide not definitely basic or acidic, whereas manganese trioxide is acidic and dimanganic heptoxide strongly acidic.

The oxides of chlorine give rise to a series of acids increasing in strength from the very weak hypochlorous acid, $HOCl$, to the strong chloric and perchloric acids, $HOClO_2$ and $HOClO_3$. Among nitrogen compounds, hyponitrous acid is very weak, nitrous acid is stronger, and nitric acid is one of the strongest acids known.

The fact that ruthenium and osmium tetroxides are not acidic, although diruthenium heptoxide is strongly acidic, is only an apparent exception to the rule. Owing to their highly saturated character, as has already been shown (p. 282), these compounds are incapable of combination with water, and cannot therefore give rise to hydrated oxides. They therefore do not come within the scope of the rule which applies to hydrated oxides only.

The Hydrogen Ion and the Catalytic Activity of Acids.

From the point of view of the theory of duplex affinity, the hydrogen atom is particularly interesting. According to the views of van den Broek and others (*Ann. Reports*, 1913, **10**, 271), the hydrogen atom is built up of a positive nucleus and one electron (compare Allen, T., 1918, **113**, 390). Consequently, the hydrogen ion $H^{\cdot}$ must consist of a positive nucleus only. The secondary negative affinity of the hydrogen ion must therefore be considered to be concentrated in a "point" of nuclear dimensions rather than distributed over the surface of a (comparatively) very large sphere. The conclusions which have been arrived at in the above discussion from the consideration of the atomic sphere will therefore not necessarily apply to hydrogen. Thus it is not essential for the production of non-polar compounds that the hydrogen atom should be surrounded by negative atoms, as in the cases of sulphur and osmium, for example (see p. 282), methane being a typical non-polar compound.

The identity of the hydrogen ion with the positive nucleus of the hydrogen atom may perhaps ultimately furnish a rational ex-

planation of the catalytic activity of acids, somewhat on the following lines.

Take a molecule $A\mathbin{\rlap{\longrightarrow}{\longleftarrow}}B$ with a tendency to dissociate according to the equation $AB \rightleftharpoons A + B$. A hydrogen ion (nucleus) if brought into contact with such a molecule will attract to itself some of the lines of force joining the electrons in A to the positive nucleus of B, or the electrons in B to the positive nucleus of A,

giving

$$\begin{array}{c}\longrightarrow A \rightleftharpoons B \longleftarrow \\ \nwarrow \ \ \nearrow \\ \mathrm{H}\end{array}$$
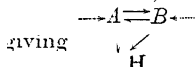
The bond uniting A to B will therefore become weaker, and the tendency of AB to dissociate will be increased. It is consequently to be expected that the hydrogen ion will accelerate a chemical change which is already taking place, or even induce a change which would not otherwise occur. Theoretically speaking, other positive ions should act in a similar manner; but since the secondary negative affinity of all other elements is distributed over the surface of a comparatively very large sphere instead of being concentrated in a "point" of nuclear dimension, the catalytic activity of other cations will be exceedingly small compared with that of hydrogen ions.

According to the theory of acids developed in the former paper (T., 1917, **111**, 253), if we neglect unsaturated affinity, the general formula for acids may be written $H\rightleftharpoons X$. If x is the value of the saturated primary affinities and y the value of the saturated secondary affinities in the formula $H\rightleftharpoons X$, y may vary from $y = x$ (the weakest possible acid) to $y = 0$ (the strongest possible acid).

If we now write the formulæ to show the unsaturated affinities, the strongest possible acid has the formula (I) and the weakest possible acid the formula (II).

$$\begin{array}{cc}\rightarrow H \longrightarrow X - & H \rightleftharpoons X \\ \text{(I.)} & \text{(II.)}\end{array}$$
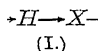
The formula (I) is the case where v (see p. 279) is vanishingly small. Strictly speaking, it is the formula of the dissociated acid ($v = 0$). The unsaturated secondary negative affinity of the hydrogen atom in a molecule of the strongest possible acid (I) is therefore equal to that of the hydrogen ion itself, and as we pass down the series through acids of decreasing strength, the unsaturated secondary negative affinity of the hydrogen atom becomes less until it vanishes, as seen in formula (II). It therefore follows that the undissociated molecule of a very strong acid should also exert catalytic activity, which catalytic activity should decrease

with decreasing strength of the acid, becoming zero in the weakest possible acid (II). It has been shown experimentally that the undissociated molecule of an acid has catalytic activity, the activity diminishing with decreasing strength of the acid (Goldschmidt and Thuesen, *Zeitsch. physikal. Chem.*, 1912, **81**, 39; Dawson and Powis, T., 1913, **103**, 2135; Dawson and Reiman, *ibid.*, 1915, **107**, 1426; Snethlage, *Zeitsch. physikal. Chem.*, 1913, **85**, 211), but according to Dawson and Powis, the activity of the undissociated acid in some cases is much greater than that of the hydrogen ion. In considering this question, it is necessary to take into account the effect of solvation.

According to the theory of duplex affinity, the chief cause of electrolytic dissociation is the combination of solute and solvent by means of unsaturated secondary affinity (see p. 280). In a solution of an acid we therefore have the following equilibria:

Undissociated molecule + solvent $\rightleftharpoons$ solvated molecule.
Solvated molecule $\rightleftharpoons$ solvated hydrogen ion + solvated anion.
Solvated hydrogen ion $\rightleftharpoons$ solvent + hydrogen ion.
Solvated anion $\rightleftharpoons$ solvent + anion.
Hydrogen ion + anion $\rightleftharpoons$ undissociated molecule of acid.

Take now the extreme case in which the secondary negative affinity of the hydrogen ion is completely saturated by the secondary positive affinity of n molecules of the solvent S (as in a very basic liquid) to give the complex ion $nS . H^{\cdot}$. The positive charge will now be distributed over the comparatively very large outer sphere of the complex (compare p. 284) instead of being concentrated in the nucleus of the hydrogen ion, and the catalytic activity of the complex will therefore be comparatively very small. Solvation will therefore reduce the catalytic activity of both hydrogen ion and undissociated molecule, and the observed catalytic activity of the hydrogen ion and the undissociated molecule in any given experiment will not be proportional to the real catalytic activity of each when unsolvated, but will depend on the degree of solvation of acid and hydrogen ion in accordance with the above-mentioned equilibria. Again, if the solvation is slight, the solvated ion and the solvated molecule may also have appreciable catalytic activity.

These principles are in agreement with the experimental observations on the relative catalytic activities of acids in different media. Water forms complexes much more readily than alcohol; therefore in aqueous solution solvation should be greater than in alcoholic solution, and the catalytic activity of acids should be less in water than in alcohol (compare Kistiakowski, *Zeitsch. physikal. Chem.*,

1898, **27**, 253, and especially Dawson, T., 1911, **99**, 1). Dawson has found that in alcoholic solutions the catalytic activity may be one hundred times as great as in water. Further, the addition of water has been found to decrease the catalytic activity in alcoholic solutions, and this has been shown to be due to combination of the water with the hydrogen ions (Goldschmidt and Udby, *Zeitsch. physikal. Chem.*, 1907, **60**, 728; Lapworth, T., 1915, **107**, 857).

It would be of considerable interest from the point of view of this paper if experiments could be made on the catalytic activity of acids in some truly non-polar medium, such as benzene or carbon tetrachloride. In such a medium, solvation and ionisation would be reduced to a minimum, because non-polar compounds are fully saturated, and therefore unable to combine with the solute. It has been shown, for instance, that benzene at 18° dissolves 2 per cent. of its weight of hydrogen chloride, and that the solution is without electrical conductivity (Falk and Walker, *Amer. Chem. J.*, 1904, **31**, 398). The catalytic activity in a truly non-polar medium would therefore be due to the unsolvated molecule only, and in the case of a very strong acid would probably be very great compared with the activity of the undissociated molecule in aqueous or alcoholic solution.

Conclusion.

For the sake of simplicity, it has been assumed throughout this paper that the atoms are spheres. It must be emphasised, in conclusion, however, that the atomic sphere so often referred to is a purely geometrical conception. We may suppose it to be a sphere described around the atom with the positive nucleus at the centre, and the radius sufficient to include all the constituents of the atom (valency electrons, etc.) within the sphere. The use of this conception is justified by the atomic volume relationships of the elements, and by the fact that the atoms are not capable of interpenetration when endowed with such small amounts of energy as correspond with the motions of thermal agitation of molecules (compare R. A. Millikan, "The Electron," pp. 139, 191).

XXX.—*Curcumin.*

By Praphulla Chandra Ghosh.

The work described in this paper was in progress, and in fact completed, before an account of the synthesis of curcumin by Lampe (*Ber.*, 1918, **51**, 1347) appeared.

A portion of the work was devoted to proving the presence of the ·CO·CH₂·CO· group, which in any case is now clear from the synthesis, confirming the formula,

$$HO \langle \quad \rangle CH{:}CH{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH{:}CH \langle \quad \rangle OH,$$
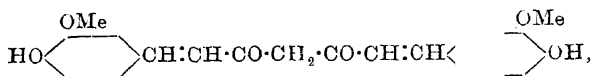
previously put forward by Milobendzki, Kostanecki, and Lampe (*Ber.*, 1910, **43**, 2163). The results bearing on this point are therefore given in an exceedingly abbreviated form.

With benzaldehyde, curcumin forms a benzylidene derivative, and it also forms a condensation product with nitrosodimethylaniline.

The action of bromine on curcumin and some of its derivatives was also studied with the object of testing the presence of two double bonds.

There were obtained *monobromocurcumin*, $C_{21}H_{19}O_6Br$, *monobromodicarbethoxycurcumin*, $C_{21}H_{17}O_4Br(O{\cdot}CO_2Et)_2$, *monobromodicarbethoxycurcumin tetrabromide*, $C_{21}H_{17}O_4Br_5(O{\cdot}CO_2Et)_2$, *dibromodicarbethoxycurcumin tetrabromide*, $C_{21}H_{16}O_4Br_6(O{\cdot}CO_2Et)_2$, *monobromodiacetylcurcumin*, $C_{21}H_{17}O_4Br(OAc)_2$, *dibromodiacetylcurcumin tetrabromide*, $C_{21}H_{16}O_4Br_6(OAc)_2$, *monobromodimethylcurcumin*, $C_{21}H_{17}O_4Br(OMe)_2$, and *dibromodimethylcurcumin tetrabromide*, $C_{21}H_{16}O_4Br_6(OMe)_2$.

In the course of this investigation, it was discovered that dicarbethoxycurcumin could be converted into dicarbethoxy*iso*curcumin simply by boiling with acetic anhydride and pyridine. This led to the view that one of the two known diacetyl derivatives of curcumin was probably diacetyl*iso*curcumin. Ciamician and Silber described a diacetylcurcumin melting at 169—170°, whilst Jackson prepared an isomeric substance melting at 154° by acetylating curcumin with acetic anhydride and sodium acetate. It was suspected that the latter was probably diacetyl*iso*curcumin, and this suspicion was found to be correct.

Jackson's compound, which can also be formed by acetylating curcumin with acetic anhydride and pyridine, gives Heller's *iso*-curcumin (*Ber.*, 1918, **47**, 887) on hydrolysis. It is therefore quite

easy to convert curcumin into *iso*curcumin. These reactions can be represented graphically, thus:

Dicarbethoxycurcumin   Curcumin

Boiling with acetic anhydride and pyridine.

Boiling with acetic anhydride and pyridine →

De-acetylated in acetic ... ution with H_2SO_4

Diacetyl compound, m. p. 154°.

Dicarbethoxy*iso*curcumin   *iso*Curcumin.

This simple conversion of curcumin into *iso*curcumin confirms Heller's view that the two substances are geometrical isomerides.

From the ferric chloride reaction, Heller considers that curcumin exists in the enolic form (I), and as there is considerable

(I.)   (II.)
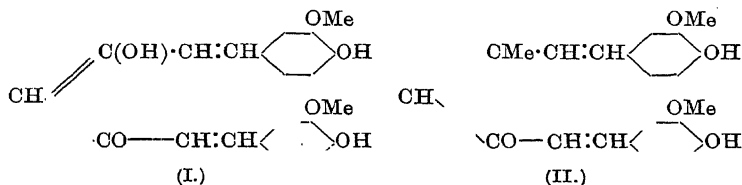
resemblance between this formula and that of *divanillylidene-mesityl oxide* (II), the latter has been prepared in the course of this investigation by condensing two molecular proportions of vanillin with one of mesityl oxide by means of hydrochloric acid, and it is intended to compare the absorption spectra of this substance with that of curcumin; similarity of absorption spectra would speak in favour of similarity of molecular configuration.

The condensation of mesityl oxide with some other aromatic aldehydes has been studied, and p-*hydroxybenzylidenemesityl oxide*, o-*hydroxybenzylidenemesityl oxide*, *piperonylidenemesityl oxide*, and *cinnamylidenemesityl oxide* have been isolated.

In connexion with the geometrical isomerism of curcumin and *iso*curcumin, there is some evidence that cinnamylidenemesityl oxide and piperonylidenemesityl oxide exist in two forms.

Most of the compounds examined in the course of this investigation are fluorescent. They are arranged in the following list in the order of their intensity of fluorescence:

Substances arranged in gradually diminishing order of fluorescence.	Solvent in which the greatest intensity is observed.
Curcumin	Chloroform.
Benzylidenecurcumin, $CHPh:C(CO\cdot CH:CH\cdot C_6H_3[OMe]\cdot OH)_2$	Acetone.
p-Hydroxybenzylidenemesityl oxide, $OH\cdot C_6H_4\cdot CH:CH\cdot CO\cdot CH:CMe_2$	Toluene
o-Hydroxybenzylidenemesityl oxide	Toluene.
Dicarbethoxycurcumin, $CH_2(CO\cdot CH:CH\cdot C_6H_3[OMe]\cdot O\cdot CO_2Et)_2$	Acetone.
Diacetylcurcumin, $CH_2(CO\cdot CH:CH\cdot C_6H_3[OMe]\cdot OAc)_2$	Acetone.
Divanillylidenemesityl oxide	Acetone.
Monobromocurcumin, $CHBr(CO\cdot CH:CH\cdot C_6H_3[OMe]\cdot OH)_2$	Acetone.
Monobromodicarbethoxycurcumin tetrabromide, $CHBr(CO\cdot CHBr\cdot CHBr\cdot C_6H_3[OMe]\cdot O\cdot CO_2Et)_2$	Chloroform.
Dibromodicarbethoxycurcumin tetrabromide, $CBr_2(CO\cdot CHBr\cdot CHBr\cdot C_6H_3[OMe]\cdot O\cdot CO_2Et)_2$	Chloroform.

From these observations, it may be inferred that (1) auxochromic groups, (2) the labile hydrogen atoms, (3) the double bonds, and (4) the symmetry of the molecule increase fluorescence, but are not the invariable factors of fluorescence.

EXPERIMENTAL.

Benzylidenecurcumin, $C_6H_5\cdot CH:C_{21}H_{18}O_6$.—A current of dry hydrogen chloride was passed through a mixture of benzaldehyde (0·5 gram), curcumin (1·8 gram), and alcohol (40 c.c.) cooled with ice. The colour became dark violet, probably owing to the formation of curcumin hydrochloride, and in about a day the whole of the curcumin dissolved and the colour changed to orange-red. After forty-eight hours, the mixture was poured into ice-cold water, when a greenish-yellow precipitate was obtained which could not be crystallised. It was purified by solution in acetic acid and fractional precipitation by sodium acetate (sample I), and subsequently in the same way by precipitation from an alcoholic solution by water (sample II). It is soluble in alcohol, acetic acid, acetone, or chloroform, shrinks slightly at 170°, and melts at 200°:

I. 0·1000 gave 0·2695 CO_2 and 0·0486 H_2O. C=73·5; H=5·4.
II. 0·1104 ,, 0·2965 CO_2 ,, 0·0527 H_2O. C=73·25; H=5·3.
$C_{28}H_{24}O_6$ requires C=73·68; H=5·26 per cent.

Condensation Product of Curcumin and Nitrosodimethylaniline, $N(CH_3)_2\cdot C_6H_4\cdot N:C_{21}H_{18}O_6$.—One part of curcumin and one part of nitrosodimethylaniline were dissolved in alcohol, two parts of zinc

chloride were added, and the mixture was warmed for a few minutes on the water-bath. When the colour became brown, the product was precipitated by water. A good deal of tarry matter was dissolved by treatment with 30 per cent. acetic acid. The residue could not be crystallised, but was purified by fractional precipitation from acetic acid solution by water. The substance obtained in this way is fairly readily soluble in alcohol, acetic acid, or acetone, shrinks at 98°, and melts and decomposes at 144—145°. Two fractions obtained by precipitation with water from acetic acid solution had the same melting point, and gave the following results on analysis:

I. 0·1502 gave 7·6 c.c. N_2 at 30° and 760 mm. N=5·7.
II. 0·1430 ,, 7·1 c.c. N_2 ,, 29° ,, 758 mm. N=5·61.
$C_{29}H_{28}O_6N_2$ requires N=5·8 per cent.

Monobromocurcumin, $C_{21}H_{19}O_6Br$.—Half a gram of curcumin was dissolved in 35 c.c. of warm chloroform, the solution cooled until curcumin began to separate, and 4·5 c.c. of a 5 per cent. solution of bromine in chloroform were then gradually added, avoiding rise of temperature. The solution became quite clear on the first addition of the bromine solution (1 c.c.), and hydrogen bromide was evolved. After ten minutes, air was blown through the mixture to drive off the chloroform, and the residual emulsion was rubbed with a little alcohol. Needle-shaped crystals of monobromocurcumin separated, which were soluble in alcohol, chloroform, acetic acid, acetone, or toluene, shrank at 131°, and melted at 136°:

0·1187 gave 0·0510 AgBr. Br=18·2.
$C_{21}H_{19}O_6Br$ requires Br=17·9 per cent.

Monobromodicarbethoxycurcumin, $C_{21}H_{17}O_4Br(O \cdot CO_2Et)_2$, prepared in a similar way from dicarbethoxycurcumin, crystallises from much alcohol in needles melting at 165—170°:

0·1172 gave 0·0382 AgBr. Br=13·87.
$C_{27}H_{27}O_{10}Br$ requires Br=13·47 per cent.

Monobromodicarbethoxycurcumin tetrabromide,

$$C_{21}H_{17}O_4Br_5(O \cdot CO_2Et)_2.$$
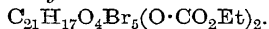
—Dicarbethoxycurcumin (1 gram) was dissolved in the minimum quantity of cold chloroform and treated with 40 c.c. of a 2·5 per cent. solution of bromine in the same solvent. After remaining at the ordinary temperature for one and a-half hours, the chloroform was driven off by a current of air. The product was extracted successively with boiling ethyl and methyl alcohols, leaving a residue which could not be crystallised, but was purified by dissolving in chloroform and fractionally precipitating with alcohol. It is

sparingly soluble in alcohol or light petroleum, and melts and decomposes at 209—210°. Different fractions gave the same analytical results:

0·1397 gave 0·1438 AgBr.   Br = 43·8.
$\qquad$ $C_{27}H_{27}O_{10}Br_5$ requires Br = 43·9 per cent.
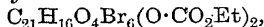
Dibromodicarbethoxycurcumin tetrabromide,
$$C_{21}H_{16}O_4Br_6(O \cdot CO_2Et)_2,$$
was obtained by brominating dicarbethoxycurcumin in cold chloroform solution with excess of bromine. It separated from alcohol in colourless crystals, softening at 148° and melting at 152°. It remains unchanged on boiling with water:

0·1278 gave 0·1460 AgBr.   Br = 48·61.
$\qquad$ $C_{27}H_{26}O_{10}Br_6$ requires Br = 48·48 per cent.

Monobromodiacetylcurcumin, $C_{21}H_{17}O_4Br(OAc)_2$.—Ciamician and Silber's diacetylcurcumin was brominated in cold chloroform solution with a little more than the theoretical quantity of a chloroform solution of bromine (as in the preparation of monobromodicarbethoxycurcumin). It crystallises from alcohol in needles melting at 173—174°, and is brighter in colour than diacetylcurcumin itself:

0·1162 gave 0·042 AgBr.   Br = 15·38.
$\qquad$ $C_{25}H_{23}O_8Br$ requires Br = 15·03 per cent.

Dibromodiacetylcurcumin tetrabromide, $C_{21}H_{16}O_4Br_6(OAc)_2$, was obtained by brominating diacetylcurcumin in cold chloroform solution with excess of bromine, and was crystallised from alcohol. It melts and decomposes at 80—83°:

0·1477 gave 0·1785 AgBr.   Br = 51·43.
$\qquad$ $C_{25}H_{22}O_8Br_6$ requires Br = 51·45 per cent.

Monobromodimethylcurcumin, $C_{21}H_{17}O_4Br(OMe)_2$, was obtained by treating dimethylcurcumin in cold chloroform solution with a little more than the theoretical quantity of bromine. It crystallises from alcohol in needles melting at 140—141°:

0·1200 gave 0·0468 AgBr.   Br = 16·6.
$\qquad$ $C_{23}H_{23}O_6Br$ requires Br = 16·49 per cent.

Dibromodimethylcurcumin tetrabromide, $C_{21}H_{16}O_4Br_6(OMe)_2$.— Dimethylcurcumin dissolved in chloroform was treated with excess of bromine, when hydrogen bromide was evolved, and, after half an hour, the chloroform was evaporated. This substance could not be crystallised, but was purified by precipitation from its hot alcoholic solution with water. Distinct fractions possessed the same melting point (softens at 96°, melts at 102—104°) and gave

identical analytical results. It is soluble in chloroform or acetic acid :

0·1120 gave 0·1437 AgBr. Br = 54·6.

$C_{23}H_{22}O_6Br_6$ requires Br = 54·87 per cent.

Conversion of Dicarbethoxycurcumin into Heller's Dicarbethoxy-isocurcumin.

A mixture of 1 gram of dicarbethoxycurcumin, 10 c.c. of acetic anhydride, and 1 c.c. of pyridine was digested at the boiling point for forty-five minutes. Alcohol (6 c.c.) and a little water were added to the cooled mixture, and the supernatant liquid was decanted from the viscous mass which thus separated. From the latter, by stirring with 2 c.c. of glacial acetic acid, a solid product was obtained, and this when crystallised from alcohol melted at 142°, which is identical with the melting point given by Heller for dicarbethoxyisocurcumin.

Found: C = 63·0; H = 5·5

$C_{27}H_{28}O_{10}$ requires C = 63·28; H = 5·46 per cent.

Acetylation of Curcumin with Acetic Anhydride and Pyridine.

Curcumin was digested with acetic anhydride and pyridine under the same conditions as described in the last paragraph, and a solid product isolated. The yellow solid obtained in this way was fractionally crystallised from acetic acid. The first fraction (which was only a minor portion) melted at 169—170°, and was found to be identical with Ciamician and Silber's diacetylcurcumin (mixed melting point). The second fraction (major portion) melted at 154°, and this, it is interesting to note, is identical with that given by Jackson for his diacetyl compound obtained by means of acetic anhydride and sodium acetate.

Found: C = 66·4; H = 5·23.

$C_{25}H_{24}O_8$ requires C = 66·37; H = 5·3 per cent.

Deacetylation of Diacetylcurcumin (m. p. 154°) and Isolation of Heller's isoCurcumin.

One gram of this diacetyl compound was dissolved in 15 c.c. of acetic acid, 1 c.c. of sulphuric acid (D 1·84) added, the mixture warmed for a minute, cooled, and poured into water. The yellow precipitate was dried on porous porcelain and extracted with hot benzene. The benzene solution, on cooling, deposited the substance as a yellow, amorphous powder, soluble in cold alcohol, acetic acid, acetone, ethyl acetate, or chloroform, sintering at 140° and melting

about 280°.   There could be little doubt that this compound was identical with Heller's *iso*curcumin:

    0·1130 gave 0·2822 CO_2 and 0·0571 H_2O.   C=68·1 ; H=5·6.

        $C_{21}H_{20}O_6$ requires C=68·4 ; H=5·43 per cent.

p-*Hydroxybenzylidenemesityl oxide,*

        $OH \cdot C_6H_4 \cdot CH:CH \cdot CO \cdot CH:C(CH_3)_2$.
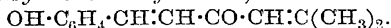
—To an alcoholic solution of 2·4 grams of *p*-hydroxybenzaldehyde and 1 gram of mesityl oxide, 1·5 grams of zinc chloride were added, and the liquid was boiled for two hours.   The solution, after concentration, was poured into water, causing the deposition of oily drops, which became crystalline on agitation.   On recrystallisation from alcohol, yellow crystals were obtained, which melted at 120° and dyed yellow shades on chrome-mordanted wool:

    0·1210 gave 0·3590 CO_2 and 0·0784 H_2O.   C=80·91 ; H=7·2.

        $C_{13}H_{14}O_2$ requires C=81·25 ; H=7·36 per cent.

o-*Hydroxybenzylidenemesityl oxide* was prepared in a similar way to the corresponding *p*-hydroxy-compound.   The crude product separated as an oil, which was obtained crystalline by dissolving in aqueous potassium hydroxide, allowing to remain for a few days, and precipitating with hydrochloric acid.   The substance dissolves with a very beautiful orange-red colour in potassium hydroxide solution:

    0·1000 gave 0·2970 CO_2 and 0·0667 H_2O.   C=81·0 ; H=7·42.

        $C_{13}H_{14}O_2$ requires C=81·25 ; H=7·36 per cent.

Piperonylidenemesityl oxide,

        $CH_2:O_2:C_6H_3 \cdot CH:CH \cdot CO \cdot CH:C(CH_3)_2$.

—Piperonal (2·6 grams) and mesityl oxide (2 grams) were dissolved in alcohol, and alcoholic potassium hydroxide was added to render the solution fairly alkaline.   The mixture was boiled for a few minutes, when an orange-coloured substance began to separate. On cooling, this solid was collected, dissolved in acetic acid, and reprecipitated with water, when it melted at 130—135° (*A*).   This proved to be a mixture of two substances melting at 148—153° and 175—178° respectively, which can be separated either by fractional precipitation by alcohol from acetic acid or by extraction with alcohol, in which the substance of higher melting point is scarcely soluble.   The hot alcoholic extract, on cooling, deposits the substance, which melts at 148—153° (*B*).   The insoluble residue, dissolved in chloroform and fractionally precipitated by alcohol (the first fraction being rejected), melted at 175—178° (*C*):

    (*A*) 0·1000 gave 0·2662 CO_2 and 0·0558 H_2O.   C=72·6 H=6·2.
    (*B*) 0·1150   ,,   0·3040 CO_2 ,, 0·0580 H_2O.   C=72·1 H=5·6.
    (*C*) 0·1021   ,,   0·2710 CO_2 ,, 0·0533 H_2O.   C=72·4   H=5·8.
        $C_{14}H_{14}O_3$ requires C=73·0 ; H=6·08 per cent.

Cinnamylidenemesityl oxide,

$$C_6H_5 \cdot CH{:}CH \cdot CH{:}CH \cdot CO \cdot CH{:}C(CH_3)_2,$$
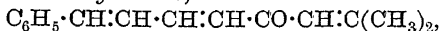
was prepared in the same way as the above piperonylidene compound. On cooling the reaction mixture, some viscous substance was deposited, from which the supernatant liquid was decanted and poured into water. The semi-solid mass was dissolved in acetic acid and precipitated with alcohol. It melts and decomposes at 180—182° (α). Addition of water to the filtrate caused the separation of a second substance, which melted and decomposed at 88° (β). Both the α- and β-compounds were soluble in alcohol, chloroform, acetone, or toluene, but could not be crystallised from any of these solvents. Experiment showed that these compounds were interconvertible; the former (α) on boiling with acetic acid for two to three minutes and adding water to the solution gave the β-compound melting at 88°, whereas the latter on boiling with alcohol for about five minutes gave, on cooling the solution thus obtained, a deposit of the α-compound melting at 180—182°.

The α-compound is less readily soluble in alcohol than the β :

(α) 0·1082 gave 0·3365 CO_2 and 0·0670 H_2O. C = 84·4; H = 6·8.
(β) 0·1494 ,, 0·4610 CO_2 ,, 0·0808 H_2O. C = 84·1; H = 6·0.
$C_{14}H_{15}O$ requires C = 84·4; H = 6·4 per cent.

Divanillylidenemesityl oxide (II, p. 293).—A current of dry hydrogen chloride was passed into an ice-cooled alcoholic solution of 2·6 grams of vanillin and 1 gram of mesityl oxide, when the liquid became deep blue. After two days, the solution was poured into cold water, the precipitate collected and triturated with sodium acetate solution. The brown, amorphous powder obtained in this way could not be crystallised, and was purified by fractional precipitation from acetic acid with water solution. It is soluble in alcohol, chloroform, or acetone, softens at 165°, and melts at 178°. Distinct fractions obtained by the above described method gave identical analytical results :

I. 0·1200 gave 0·316 CO_2 and 0·067 H_2O. C = 71·8; H = 6·2.
II. 0·1065 0·282 CO_2 0·059 H_2O. C = 72·21; H = 6·1.
$C_{22}H_{22}O_5$ requires C = 72·1; H = 6 per cent.

I take this opportunity of thanking Prof. B. N. Das for his kind help and encouragement during the progress of the work.

XXXI.—*The Rotatory Dispersive Power of Organic Compounds. Part IX. Simple Rotatory Dispersion in the Terpene Series.*

By Thomas Martin Lowry and Harold Helling Abram.

In a paper on "The Form of the Rotatory Dispersion Curves," published in 1913 (T., **103**, 1067), it was shown :

(*a*) That the rotatory dispersion in a large number of simple organic compounds may be expressed by the formula

$$\alpha = k / (\lambda^2 - \lambda_0^2),$$

where k is the "rotation constant" and λ_0^2 is the "dispersion constant" of the substance.

(*b*) That this formula can be applied both to magnetic and to natural rotatory powers.

(*c*) That a very simple method of testing the form of the dispersion curves is to plot the reciprocals of the rotatory powers against the squares of the wave-lengths. When the simple dispersion formula is valid, the observations will plot out to a straight line.

The validity of this simple dispersion formula was established in several ways. Thus :

(1) Twenty-five hydrocarbons, alcohols, and acids for which the ratio $\alpha_{4358} / \alpha_{5461} = 1\cdot636$ were grouped together, and their *magnetic* dispersion ratios were averaged for six different wave-lengths ; these averages showed a remarkable agreement with the ratios calculated by means of the simple dispersion formula.

(2) In the same way the *optical* dispersion ratios of eight secondary alcohols, for which $\alpha_{4968} / \alpha_{5461} = 1\cdot651$, were found to agree closely with ratios calculated by the simple formula.

(3) A few optical and magnetic rotations of larger magnitude showed a similar close agreement in individual cases, without the necessity for averaging which arises when the readings are small.

(4) In the case of α- and β-methyl glucosides, very concordant results were obtained when the two constants of the simple equation were calculated (*a*) from the mercury readings α_{4358} and α_{5461}, (*b*) from the cadmium readings α_{5086} and α_{6438} (Lowry and Abram, *Trans. Faraday Soc.*, 1914, **10**, 108).

These earlier observations showed that the simple dispersion formula can be applied very generally to compounds of simple structure, such as the optically active secondary alcohols, which contain only a single asymmetric carbon atom and also to com-

pounds such as the glucosides which contain several asymmetric carbon atoms associated with the simplest possible radicles, for example, hydrogen, hydroxyl, and the like. An opportunity has, however, occurred recently of testing the validity of this same simple formula in the case of a large number of optically active compounds in which these elements of simplicity in the molecular structure are conspicuously absent. The striking results of this further test form the subject of the present communication.

The new data now under consideration were provided by the observations of Prof. Rupe, who in continuation of earlier experiments on the "Influence of Constitution on the Rotatory Power of Optically Active Substances" (*Annalen*, 1903, **327**, 157; 1909, **369**, 311; 1910, **373**, 121; 1913, **395**, 87, 136; 1913, **398**, 372; 1914, **402**, 149) has published a series of measurements of the optical rotatory power of (1) twelve derivatives of methylenecamphor, (2) menthol and eleven of its esters, (3) myrtenol and eleven of its esters, (4) three hydrocarbons derived from citronellaldehyde, (5) camphor, pulegone, and carvone (*Annalen*, 1915, **409**, 327). Unlike the previous series of measurements, which were confined to observations with sodium light, the last series included, in the case of almost every compound, readings for four different wave-lengths in the visible region of the spectrum. It was therefore possible to study, not only the optical rotatory power of the various compounds, but also the character of their rotatory dispersion.

The four wave-lengths, selected from a continuous spectrum, were $\lambda = 6563$, 5898, 5463, and 4861, corresponding closely with the Fraunhofer lines: $C = 6563$, $D = 5893$, $F = 4861$, and the green mercury line Hg 5461. In order to preserve a convenient sequence of lettering, these four wave-lengths were described as C, D, E, and F; but, as the symbol E has long been applied to the Fraunhofer line of wave-length 5270, the symbol Q is used below for the green (quicksilver) line in the series, which thus becomes C, D, Q, F.

The various substances were examined either in the pure state as liquids at $20°$ or dissolved in benzene at $20°$, since this solvent was found to have no very great influence on the rotatory powers; several substances were examined both in the pure state and in solution.

When the experimental work was approaching completion, the data were handed over for detailed analysis to Dr. A. Hagenbach, Professor of Physics in the University of Basle. The important deductions which he was able to make are set out in a paper on "Rotatory Dispersion in Homologous Series" (*Zeitsch. physikal.*

N*

Chem., 1915, **89**, 570). The chief points of this paper are as follows:

(1) The dispersion ratio a_F/a_C is practically constant in each series of closely-related compounds. Compounds which differ in any marked degree from the average are regarded as "relatively anomalous."

(2) A similar statement may be made in reference to all the six ratios a_F/a_C, a_F/a_D, a_F/a_Q, a_Q/a_C, a_Q/a_D, a_D/a_C, as was shown by tabulating these ratios for (i) eight derivatives of methylene-camphor, (ii) menthol and seven of its esters, (iii) three hydro-carbons from citronellaldehyde.

(3) It follows, therefore, that if the dispersion law for one member of the series be given by the equation $a = \phi(\lambda)$, the rotatory dispersion in every compound may be expressed by equations, such as:

$$[a_1] = C_1 \phi(\lambda).$$
$$[a_2] = C_2 \phi(\lambda).$$
$$[a_3] = C_3 \phi(\lambda).$$

This proportionality of rotatory powers was demonstrated by tabulating the ratios a_2/a_1, a_3/a_1, a_4/a_1, etc., in each of the three series of compounds.

Attempts were made to determine, mainly by graphical methods, the nature of the unknown function $\phi(\lambda)$. Thus, the equations of Biot,

$$a = B/\lambda^2,$$

and of Stefan,

$$a = A + B/\lambda^2,$$

were tested by plotting a against $1/\lambda^2$. Boltzmann's equation:

$$a = A/\lambda^2 + B/\lambda^4 \quad \text{or} \quad a\lambda^2 = A + B/\lambda^2,$$

was tested by plotting $a\lambda^2$ against $1/\lambda^2$. In neither case was an exact linear law disclosed. The equations of Lommel, and the two-term equation which Drude used to express the rotatory power of quartz, could not be tested in this way; but the empirical equations:

$$a = A + B/\lambda^n \quad \text{and} \quad \log a = A + B/\lambda$$

were tested by plotting $\log a$ against $\log 1/\lambda$ and against $1/\lambda$; subsequently, $\log a$ was also plotted against λ, and a against $1/\lambda$ (*Annalen*, 1915, **409**, 349, 351), but again without disclosing any simple linear relation between these quantities. The nature of the function in the equation $a = \phi(\lambda)$ thus remained still undiscovered. The present paper serves to supply this deficiency by showing that in almost every case the new dispersion data can be

expressed by a simple equation of the type first put forward by Drude.

The fact that Drude's equation was not used by Hagenbach, and in general failed during many years to secure the practical recognition which it deserves, may be accounted for in two ways. In the first place the equation was put forward, as an approximation only, in a very general form:

$$\alpha = \Sigma \frac{k_n}{\lambda^2 - \lambda_n{}^2},$$

containing an indefinite number of arbitrary constants. The arbitrary constants, $\lambda_1{}^2$, $\lambda_2{}^2$, $\lambda_3{}^2$, . . ., in the denominator were deduced from measurements of refractive dispersion, and it was not even suggested that they could be derived (in a still more satisfactory way and often with much greater exactness) from the rotations themselves. In the second place, Drude demonstrated the validity of his equation only in one single case, namely, that of quartz, the equation for which took the form

$$\alpha = \frac{k_1}{\lambda^2 - \lambda_1{}^2} \qquad \frac{k}{\lambda^2}.$$

No data whatever were given for optically active liquids, and the magnetic rotatory dispersion in carbon disulphide and in creosote (!) was expressed by a different formula, also depending on measurements of refractive dispersion. The first extensive practical application of Drude's formula was therefore made less than six years ago in the second paper of the present series.

The easiest (although perhaps the least exact) method of testing the simple dispersion law, $\alpha = k/(\lambda^2 - \lambda_0{}^2)$, is to plot the reciprocals of the rotations against the squares of the wave-lengths. The dramatic effects which are produced by plotting $1/\alpha$ against λ^2 are shown by comparing the straight lines of Figs. 1 to 4 with the broken lines* or curves which were given by all other methods of plotting. It is specially remarkable that plotting α against $1/\lambda^2$ (Stefan's formula) should give curves, where plotting $1/\alpha$ against λ^2 (Drude's formula) gives very exact straight lines. These lines indicate clearly that, where half a dozen other relationships have failed, the simple Drude formula gives at once a satisfactory expression of the experimental data.†

* Hagenbach appears to have plotted his curves on the assumption that the "E" line used by Rupe was the Fraunhofer line α_{5270}, and not the mercury line α_{5461}.

† More exact data may perhaps compel the use of additional terms, as in the case of quartz, which requires one, two, or three terms, according to the range and accuracy of the data employed, but there are no indications of this in the data examined hitherto.

A marked exception occurs in the case of pulegone, which gives a smooth, full curve, and evidently shows " complex " rotatory dispersion.   Diphenylmethylenecamphor, $C_{10}H_{14}O{:}CPh_2$, the dispersion ratios of which are much lower than those of all the related compounds, gives a curve; so also does menthyl β-phenylcinnamate, $C_{10}H_{19}O{\cdot}CO{\cdot}CH{:}CPh_2$, the rotatory dispersion of which must be complex, since the dispersion ratio, $a_F/a_C = 1{\cdot}72$, falls below the

FIG. 1.
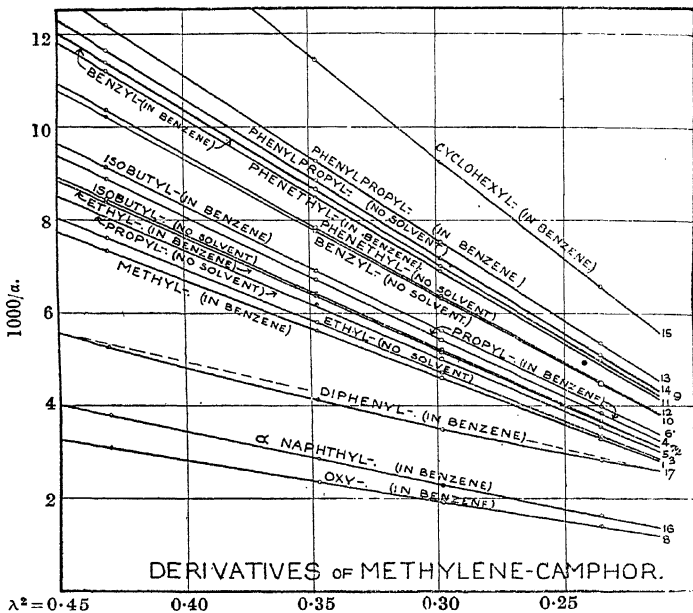
Rotatory dispersion in derivatives of methylenecamphor.

Notice curvature in the case of the diphenyl derivative.

minimum value $a_F/a_C = \lambda_C^2/\lambda_F^2 = 1{\cdot}818$, beyond which λ_0^2 would become negative and λ_0 an imaginary quantity; the fact that both these compounds contain the group $:CPh_2$ can at present only be regarded as a coincidence.   All the other compounds appear, as a result of this rough graphical analysis over a narrow range of wave-lengths, to give simple rotatory dispersion.

A more exact test of the dispersion formula is given by numerical calculation.   The following table shows that the specific rotations,

observed and calculated, of a series of typical compounds lie well within the range of possible experimental errors.

TABLE I.

Specific Rotations, Observed and Calculated.

Ethylidenecamphor,* $[\alpha] = 47 \cdot 322/(\lambda^2 - 0 \cdot 0829)$.

Obs.	136·37°	178·58°	219·31°	308·49°
Calc.	136·05	178·58	219·55	308·49
O—C	+0·32	±	−0·24	±

Hydroxymethylenecamphor,* $[\alpha] = 22 \cdot 843/(\lambda^2 - 0 \cdot 0874)$.

Obs.	66·53	87·66	108·57	153·41
Calc.	66·53	87·70	108·26	153·41
O—C	±	−0·06	+0·33	±

Benzylmethylenecamphor, $[\alpha] = 33 \cdot 431/(\lambda^2 - 0 \cdot 0887)$.

Obs.	97·87	129·00	156·26	226·50
Calc.	97·75	129·00	156·39	226·50
O—C	+0·12	±	−0·13	±

Menthol,* $[\alpha] = 15 \cdot 068/(\lambda^2 - 0 \cdot 0236)$.

Obs.	37·01	46·58	54·78	70·84
Calc.	37·01	46·47	54·82	70·84
O—C	±	+0·11	−0·04	±

Menthyl benzoate,* $[\alpha] = 29 \cdot 364/(\lambda^2 - 0 \cdot 0255)$.

Obs.	72·41	91·10	107·76	139·30
Calc.	72·46	91·10	107·59	139·30
O—C	−0·05	±	+0·17	±

Myrtenol, $[\alpha] = 14 \cdot 700/(\lambda^2 - 0 \cdot 0316)$.

Obs.	36·83	46·49	55·04	71·81
Calc.	36·83	46·48	55·09	71·81
O—C	±	+0·01	−0·05	±

Myrtenyl benzoate, $\alpha = 11 \cdot 505/(\lambda^2 - 0 \cdot 0341)$.

Obs.	29·01	36·67	43·51	56·90
Calc.	29·01	36·67	43·52	56·90
O—C	±	±	−0·01	±

* Dissolved in benzene.

In view of the fact that the readings for solutions in benzene were multiplied by ten to convert them into specific rotations, whilst the others were approximately doubled, the agreement shown above is practically perfect.

Even clearer evidence of the validity of the simple dispersion formula is afforded by a study of the average dispersion ratios observed and calculated for groups of related compounds. Three such groups were averaged by Hagenbach, namely :

(*a*) Eight derivatives of methylenecamphor (dissolved in benzene), $a_F/a_C = 2 \cdot 310$.

(*b*) Seven esters of menthol (pure or in benzene), $a_F/a_C = 1 \cdot 920$.

FIG. 2.
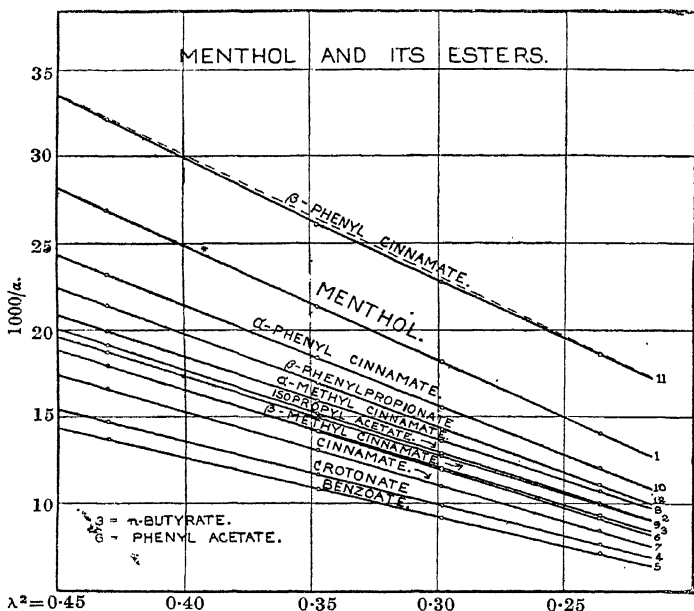
Rotatory dispersion in menthol and its esters.

Notice curvature in the case of β-phenylcinnamate.

(*c*) Three derivatives of citronellaldehyde (in the pure state), $a_F/a_C = 1 \cdot 991$.

To these there are now added average ratios for :

(*d*) Six derivatives of methylenecamphor (in the pure state), $a_F/a_C = 2 \cdot 303$.

(*e*) Menthol and seven esters (dissolved in benzene), $a_F/a_C = 1 \cdot 911$.

(f) Myrtenol and eight esters (in the pure state), $a_F/a_G = 1.958$.
The close agreement between the observed and calculated values of these ratios is shown in table II.

Fɪɢ. 3.

MYRTENOL AND ITS ESTERS.

Rotatory   *in myrtenol and its esters.*
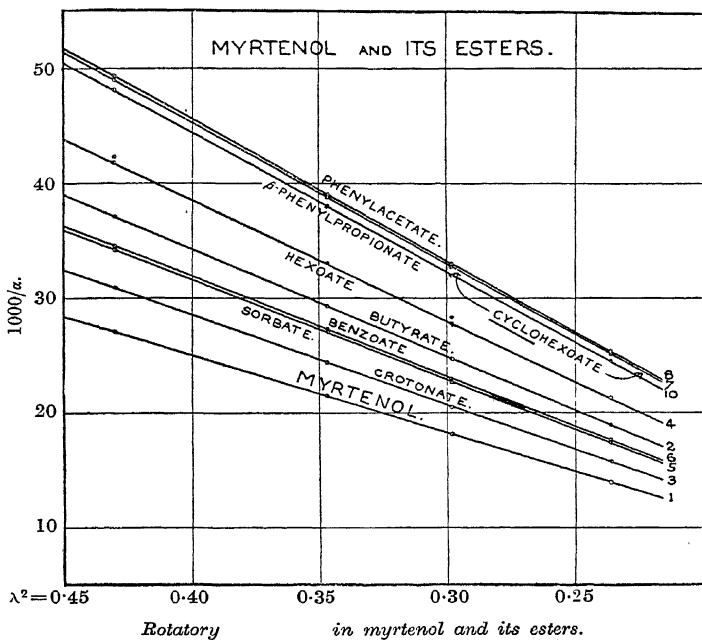
Tᴀʙʟᴇ II.

Dispersion Ratios, Observed and Calcu

		a_F/a_C.	a_F/a_D.	a_F/a_Q.	a_Q/a_C.	a_Q/a_D.	a_D/a_C.
(a)	Obs.	2·310	1·751	1·415	1·633	1·237	1·319 } $\lambda_0{}^2=$
	Calc. ...	2·310	1·752	1·418	1·629	1·236	1·318 } 0·0879
(b)	Obs.	1·920	1·529	1·294	1·488	1·181	1·259 } $\lambda_0{}^2=$
	Calc. ...	1·921	1·529	1·294	1·484	1·181	1·257 } 0·0250
(c)	Obs.	1·991	1·561	1·313	1·515	1·188	1·274 } $\lambda_0{}^2=$
	Calc. ...	1·992	1·569	1·316	1·513	1·191	1·269 } 0·0401
(d)	Obs.	2·303	1·756	1·423	1·619	1·234	1·312 } $\lambda_0{}^2=$
	Calc. ...	2·303	1·748	1·417	1·626	1·234	1·318 } 0·0871
(e)	Obs.	1·911	1·521	1·289	1·482	1·180	1·256 } $\lambda_0{}^2=$
	Calc. ...	1·911	1·522	1·292	1·479	1·179	1·255 } 0·0227
(f)	Obs.	1·958	1·550	1·306	1·499	1·186	1·264 } $\lambda_0{}^2=$
	Calc. ...	1·958	1·550	1·306	1·499	1·186	1·264 } 0·0334

This agreement is nearly as close as in the case of the data by which the validity of the simple Drude formula was first established, and even the largest differences are usually less than the average errors of the individual ratios. The "simple" character of the rotatory dispersion could therefore only be called in question if data were available of greater exactness or over a wider region of the spectrum.

A further opportunity of testing the validity of the simple dis-

FIG. 4.
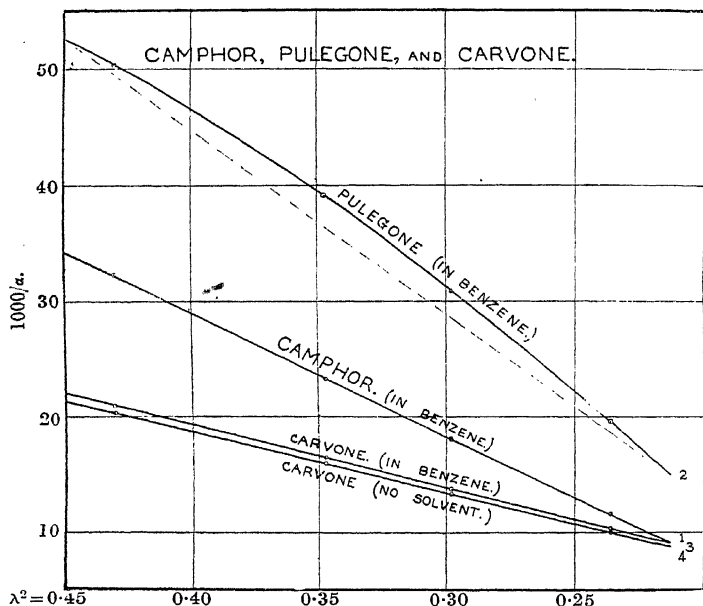
Rotatory dispersion in derivatives of camphor pulegone and carvone.
Notice curvature in the case of pulegone.

person law is provided by the inclusion in a more recent paper by Prof. Rupe (*Helv. Chim. Acta*, 1918, **1**, 452) of dispersion data for four samples of camphylcarbinol,

$$C_8H_{14} \diagdown \begin{array}{c} CH \cdot CH_2 \cdot OH \\ | \\ CO \end{array} ,$$
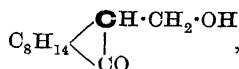
a compound containing three asymmetric carbon atoms as com-

ponents of a complex ring system. The agreement between the observed and calculated rotations is shown in table III.

TABLE III.

Rotatory Dispersion in Camphylcarbinol.

First sample, $[\alpha] = 15\cdot980/(\lambda^2 - 0\cdot10220)$.

	$\lambda = 6563$	5898	5463	4861
Obs.	$48\cdot64°$	$65\cdot24°$	$81\cdot57°$	$119\cdot17°$
Calc.	$48\cdot64$	$65\cdot05$	$81\cdot43$	$119\cdot17$
O—C	$\pm$	$+0\cdot19$	$+0\cdot14$	$\pm$

Second sample, $[\alpha] = 15\cdot213/(\lambda^2 - 0\cdot10223)$.

Obs.	$46\cdot31$	$62\cdot11$	$77\cdot67$	$113\cdot48$
Calc.	$46\cdot31$	$61\cdot93$	$77\cdot53$	$113\cdot48$
O—C	$\pm$	$+0\cdot18$	$+0\cdot14$	$\pm$

Third sample, $[\alpha] = 15\cdot252/(\lambda^2 - 0\cdot10239)$.

Obs.	$46\cdot45$	$62\cdot22$	$77\cdot74$	$113\cdot90$
Calc.	$46\cdot45$	$62\cdot13$	$77\cdot79$	$113\cdot90$
O—C	$\pm$	$+0\cdot09$	$-0\cdot05$	$\pm$

Fourth sample, $[\alpha] = 16\cdot10/(\lambda^2 - 0\cdot10304)$.

Obs.	$49\cdot13$	$65\cdot73$	$82\cdot44$	$120\cdot82$
Calc.	$49\cdot13$	$65\cdot76$	$82\cdot39$	$120\cdot82$
O—C	$\pm$	$-0\cdot03$	$+0\cdot05$	$\pm$

It will be observed that the sample having the highest rotatory power, which was also probably the purest, gives a remarkably close agreement, the differences being in opposite directions and amounting only to a few hundredths of a degree, or about 1 part in 2000. This exact agreement suggests that the simple dispersion law may be of value as a test of purity, and that deviations from it may in some cases justify a further examination of the chemical composition of the material used for the measurements.

It is of interest to notice the chemical character of the compounds to which the "simple" dispersion formula has now been applied. They are as follows:

1. Methylene camphors.   2. Menthol esters.   3. Myrtenol esters.
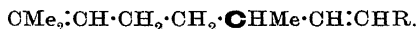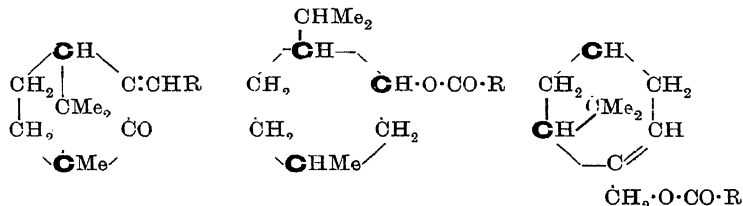
$$CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe{\cdot}CH{:}CHR.$$
4. Hydrocarbons from citronellaldehyde.

Nearly all are complex ring compounds or loaded with double bonds. The fact that the simple formula applies to compounds of such complex structure is remarkable evidence of the broad and sound basis on which the formula rests.

Characteristic Wave-lengths.—In Drude's simple equation, the rotatory dispersion is defined completely by the "dispersion constant" λ_0^2; this is the square of a wave-length, which is that of a hypothetical absorption band, usually in the ultra-violet region of the spectrum. This wave-length defines the whole course of the dispersion curve, and is independent of the particular wave-lengths used to determine it; thus the value of λ_0^2 may be deduced equally well from the mercury ratio a_{4358}/a_{5461}, from the cadmium ratio a_{5086}/a_{6438}, or from the ratio a_F/a_C derived from the data now under discussion. A preliminary study of these data by Prof. Rupe had, however, disclosed the fact that, in the case of the methylene-camphors, $a_F/a_C = a_D$, whilst in the case of the citronellaldehyde hydrocarbons, $a_F - a_C = a_C$, that is, for each series there is a "characteristic wave-length," λ_a (*Zeitsch. physikal. Chem.*, 1915, **89**, 581), for which the rotation is equal to the difference between the rotations for the F and C lines. This wave-length is not a fundamental constant of the dispersion curve like the λ_0^2 of Drude's equation, since it depends on the two standard wave-lengths, for example, F and C, which are selected as determining the difference; but it usually lies within the limits of the visible spectrum and affords a picturesque method of setting out the essential features of the dispersion curve. By assuming the validity of Stefan's formula, Hagenbach showed that this wave-length can be deduced from the expression

$$\frac{1}{\lambda_a^2} \qquad \frac{a_C}{-a_C} \left\{ \frac{1}{\lambda_F^2} - \frac{1}{\lambda_C^2} \right\} - \frac{1}{\lambda_C^2}$$

or, taking in all the four rotatory powers,

$$\frac{1}{\lambda_a^2} = \frac{a_F - a_C - a_E}{a_C - a_D} \left\{ \frac{1}{\lambda_C^2} - \frac{1}{\lambda_D^2} \right\} - \frac{1}{\lambda_F^2}.$$

Drude's equation, on the other hand, which is the one that actually fits the curves, gives for the "characteristic wave-length" the expression

$$\lambda_a^2 = \frac{\lambda_C^2 - (n-2)\lambda_F^2}{(n-1)^2} = \frac{0.4307 - 0.2363(n-2)}{(n-1)^2},$$

where n is the dispersion ratio a_F/a_C. Thus, for the citronell-aldehyde hydrocarbons, for which $n = 2.00$, this equation gives $\lambda_a^2 = \lambda_C^2$, as was observed experimentally when it was found that $a_F - a_C = a_C$.

Constant Rotatory Dispersion in Homologous Series.—In the compounds now under consideration, new radicles are introduced into the molecule at points which are separated from the asymmetric carbon atoms by a considerable chain, including in every case either an oxygen atom or a double bond. A constant dispersion ratio is therefore observed from the beginning, and any substance of which the rotatory dispersion differs largely from the average of the series is noteworthy and exceptional. The only conspicuous exceptions amongst some thirty-six compounds under consideration in the present research were found in two substances containing the group $:CPh_2$. These have now been shown to differ from the others also in giving complex instead of simple dispersion curves, so that the rule appears to apply without exception to all compounds showing simple rotatory dispersion.

A different state of affairs prevails, however, in the secondary alcohols of Pickard and Kenyon, which have a "growing chain" attached directly to the asymmetric carbon atom. The dispersion is here always simple, but the dispersion constant varies in the different series, and only assumes a steady value in each series when the "growing chain" of carbon atoms has definitely established itself as the heaviest radicle attached to the asymmetric carbon atom (Lowry, Pickard, and Kenyon, T., 1914, **105**, 101). The lowest homologues usually show an exceptionally high rotatory dispersion, but this is not accompanied by any change in the type of the dispersion curve, and is therefore entirely distinct from the "anomalous rotatory dispersion," of which an exact definition was given in a former paper of the present series (T., 1915, **107**, 1195). It would be a real misfortune if substances which are perfectly normal in their rotatory dispersion were to be regarded even as "relatively anomalous" whenever they happen to differ slightly from their homologues, and it is hoped that this unnecessary and misleading description will be abandoned.

Summary.

It is shown that the simple dispersion formula
$$\alpha = k / (\lambda^2 - \lambda_0^2)$$
can be applied to express the rotations produced by a large number of compounds of the terpene series, including (*a*) derivatives of methylenecamphor, including camphylcarbinol, (*b*) menthol and its esters, (*c*) myrtenol and its esters, and (*d*) hydrocarbons derived from citronellaldehyde. Pulegone, and two compounds containing the group $:CPh_2$, show complex rotatory dispersion.

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XXXII.—*A New Sector Spectrophotometer.*

By SAMUEL JUDD LEWIS.

IN a paper by the author on "The ultra-violet absorption spectra of blood sera" (*Proc. Roy. Soc.*, 1917, [*B*], **89**, 327), it was stated that the work described had been done with two sector spectrophotometers, that these were not adequate to the exacting nature of the investigation, although they were the best and most modern instruments available, and that a new photometer to the author's design was under construction. That apparatus has now been in use for several months, and the purpose of this paper is to describe it. A short account of the method of using such instruments is given in the reference mentioned above.

As was the case with the work detailed in the paper cited, the present development of the sector spectrophotometer has been generously supported by the Beit Research Fund Committee, the trustees of a fund which has been placed at the disposal of the British Homeopathic Association by Mr. Otto Beit for purposes of scientific research.

The new instrument was designed by the author in 1915 with a view to meeting the requirements of the work on blood serum. No instrument can be unnecessarily refined for this, and should it be desired to employ the method of ultra-violet absorption spectrography for clinical purposes, whether for blood serum or for any other substances, an instrument which is at once trustworthy and easy to manipulate is essential. Incidentally, an instrument which fulfils these conditions should satisfy most of the demands of scientific research and bring the practice of ultra-violet absorption spectroscopy within the range of applied chemistry. Unless or until the ideals set out are attained, absorption spectroscopy can have little more than academic significance; but perfect, easily adjustable spectrophotometers may be expected in course of time to occupy a place in the general laboratory not less important than that filled by the polarimeter or the refractometer.

Among the objects aimed at in the new design were the following:

(*a*) The utmost accuracy and refinement in the resulting spectra, because for the serum work it is required to discover with certainty very small differences of detail in the absorption curve, as explained in the paper cited.

(*b*) To work quickly as well as accurately, since it is necessary to undertake the examination of a serum at very short notice, and there is no reasonable opportunity of revising the observation, as
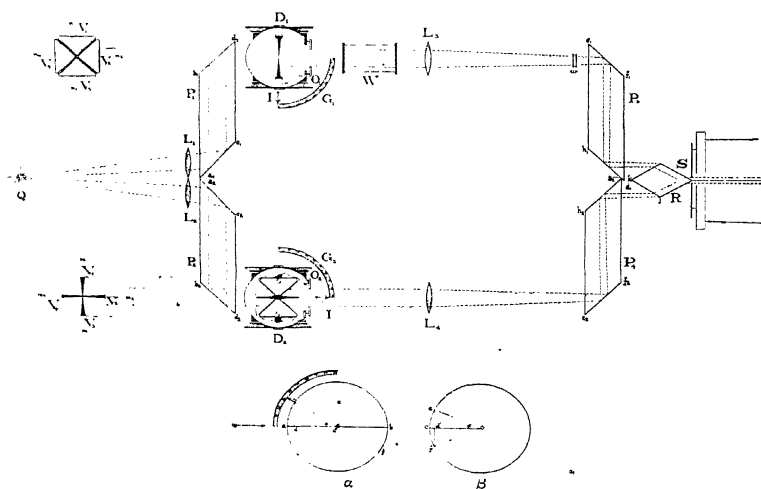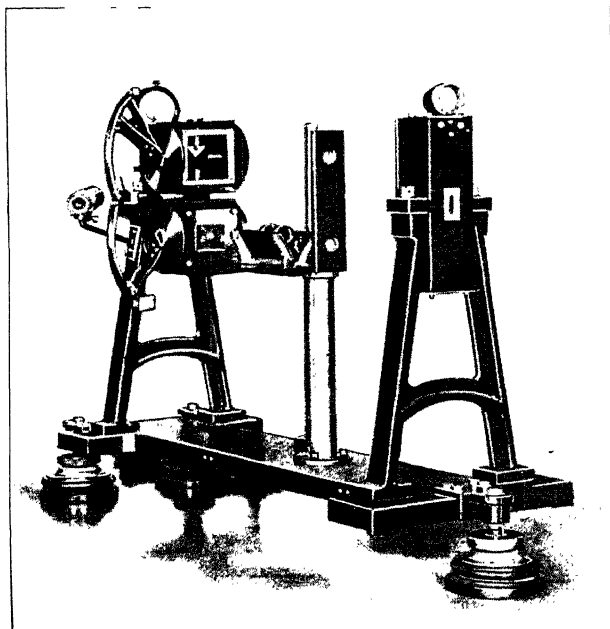
the serum will usually have changed in character by the time the absorption curve is drawn; this presumes quick and perfect adjustment of the instruments.

(c) To maintain this excellent adjustment throughout an experiment, or to restore it from time to time during the progress of an observation, without the necessity of other disturbances.

(d) Precise quantitative values for the extinction coefficients, since the amplitude of the curve has important significance.

(e) To attain this high standard, and yet to be able to use the one spectrograph alternately with the photometer and for other purposes as circumstances may require.

The photograph exhibits the general appearance of the new photometer; it exposes the vanes in the upper sector, the front of the sector box having been removed; also only one platform bearing a tube carrier is shown. The arrangement of parts is displayed in the diagram.

Q represents a suitable lamp, light from which falls on the two lenses L_1, L_2, which render the light parallel. These pencils of light pass through the face a_1b_1·in the reflecting prism P_1 and through the face a_2b_2 in the reflecting prism P_2 in the manner shown, and are reflected approximately at right angles by the inclined faces a_1c_1 in prism P_1 and· a_2c_2 in the prism P_2, so that in each case the light follows a course parallel to the main axis of the prism to a second inclined face b_1d_1 in prism P_1 and b_2d_2 in prism P_2, where it is reflected again at right angles.

The parallel beam reflected from b_1d_1 passes through the sector D_1, the diaphragm O_1, and the lens L_3 to the inclined face e_1f_1 in reflecting prism P_3, where it is reflected at right angles along the main axis of the prism on to the inclined face g_1h_1, where it is again reflected at right angles and passes out of the prism on to the face ki of the rhomb R placed in front of the slit S of the spectrograph, or, in the absence of the rhomb, directly on to the slit.

The pencil from b_2d_2 undergoes similar treatment, and eventually passes out of the photometer on to the face kj of the rhomb.

The rhomb may be dispensed with if the pencils of light are directed so as to fill the angles of the prisms at g_1 and g_2, provided that one prism slightly overlaps the other, as shown in the figure, so that the prominent edge may define the line of juxtaposition. It will be seen that any stray parts of the pencils of light would be reflected or escape out of the field.

The essential part between the two prisms in either path is the sector D_1, D_2, capable of cutting off any desired portion of the light passing along that path.

It should be observed that the prisms and sectors are enclosed in dust-proof metal boxes provided with quartz windows.

The sector system is placed in a part of the path where the light is parallel. It consists of four vanes, V_1, V_2, V_3, V_4, as shown in the side elevations in the figure. Each vane has two edges at right angles, and when the four vanes are disposed to one another in one plane, so that the four angles meet at a point, the system is closed and no light can pass. This arrangement is represented in the upper path in the figure. The common point of the four angles is on the optic axis, to which the plane is at right angles. Each vane can be turned by means of suitable mechanism about its bisectors, m_1, m_2, m_3, m_4. When all the vanes are turned simultaneously through an angle of 90° about their respective bisectors, light can pass in the direction of the optic axis without any interruption except that caused by the slight obstruction due to the thickness of the material of the vanes, as shown in the figure for the lower path. By turning the vanes through any other given angle about their bisectors, a known proportion of the light may be allowed to pass. Each of the four vanes is carried on a wheel, by means of a spindle which coincides with the bisector of the vane and also forms the axle of the wheel. These wheels are mounted on the outside of the walls of the box enclosing the sector at right angles to one another, and fit into one another by bevelled cogs. They move simultaneously, and the fitting is so close that back-lash is reduced to an insignificant minimum. The amount of rotation of the vanes is measured by a pointer, I, mounted on the front wheel and moved against an arc graduated in half degrees from 0 to 90.

A diaphragm or stop, O_1, O_2, is placed in front of each sector to reduce the section of the beam of light to suitable dimensions, say 9 mm. in diameter when the observation tubes or cells have a lumen of 12 mm.

In order to correct the error caused by the obstruction due to the thickness of the material of the vanes, their edges are reduced to knife edges, and the thickness along the bisector is graduated from the minimum at its extremity at the optic axis to what is necessary, say 1 mm., at a distance of 10 mm. The two sides of each vane are equally made, and each of the four surfaces is plane or concave. Hence a section through a vane at right angles to its bisector has the form of a rhombus having two very obtuse and two very acute angles; also a section which includes the bisector has the form of an isosceles triangle.

It follows that when the sector system is open, as shown in the lower path in the figure, the obstruction or shadow produced by

each vane has the form of a geometrical sector of known dimensions, and therefore the sectional area of the pencil of light passing through the sector system is reduced by four times the area of one small sector shadow; also, each of the four apertures has the form of a geometrical sector.

Compensation for this reduction in area is made by employing for the path in which the light is to be of whole, or 100 per cent. intensity, that is, for the path in which the substance under observation is placed, a diaphragm the aperture of which is appropriately larger than that of the diaphragm in the other path.   In the author's instrument, the diameter of the larger aperture is 9·3 mm. and that of the smaller 9·0 mm.   These diaphragms are loose and may be used with either sector, according to whether it is desired to use the upper or lower sector.

The only limitation to this arrangement is that the sectors do not operate for those angles which are included by the small angle covered by the thickness of the vanes.   In the author's instrument this is 2·6°, so that the range of operation is from 2·6° to 90°.

The lenses L_3, L_4, placed between the sectors and the second set of prisms, focus the light on the slit, the focus being that for light of a wave-length of about 3000.

The edge of the rhomb is placed close to the slit, so that the two pencils of light when they emerge from either side of it into the slit may be at the focus of the collimating lens; the line of juxtaposition between the two spectra is thus very clearly defined without the least overlapping or intervening space, with the result that the lines in the two spectra, whether visual or photographic, can be compared for their relative intensities at the best advantage.

The cell containing the substance under observation is placed in the parallel beam of light between the sector and the central lens; room is provided for tubes up to 100 mm. in length, and tubes of this length were used successfully in an investigation relating to Lambert's law.   As the pencil of light is 9·3 mm. in diameter, it is desirable for long tubes that the lumen of the tube should be at least 12 mm. in diameter, so as to avoid serious reflection from the inner walls of the tube.   When the lumen is small and the layer of substance thin, it may be placed in the convergent beam immediately in front of the prism P_3, as shown at w, and a still smaller cell might be interposed between the prism P_3 and the face ki of the rhomb, but only with due regard to existing conditions.   Inasmuch as the system in the lower path of light is identical with that in the upper, the cell may be placed in the lower with equal advantage, or, as explained later, cells may be placed in both beams simultaneously.

The new instrument is characterised chiefly by its sectors; these are distinguished both in their construction and in the principles upon which they operate. In comparison and contrast with other sectors, they accommodate the whole beam of light, and not merely half, as is the case with some others; this enables exposures to be reduced to one-half in order to produce a photograph of the same intensity; the exposures being continuous, calibration of the photographic plate is avoided; the direct function of the new sectors is to cut down the intensity of the light, and not to do so indirectly by altering the exposure, as is the case with the Hilger instrument; the sector is still, which is a great convenience. The whole aperture of the sector system is made up of four sector-shaped apertures arranged diagonally about the optic axis, that is, they are disposed at an angle of 45° to the vertical. This has the advantage of utilising all parts of the circular beam of light in proper proportion, whatever the magnitude of the effective aperture at the moment. In this it differs from the iris and other forms of stop or sector, which reduce the intensity of the light by cutting down the light from the periphery of the beam inwards, or by cutting it down in some other way which assumes that every part of the field is equally illuminated. Under the conditions of ordinary practice, this assumption lacks sufficient justification where precise photometry is required.

The size of the sector aperture is measured in terms of the angle which it forms at the optic axis. The angle 45° represents an aperture of 100 per cent., and the angle formed at the optic axis by the shadow cast by one half of a vane in any given position is ϕ. Hence the sector aperture is proportional to $45° - \phi$. This method of measuring the size of the aperture is exceedingly convenient both for simplicity of calculation from the angle θ, which is read on the graduated arc, and for the fact that apertures of any odd value may be produced at will. This will become evident from the following explanation of the manner of calculation.

When the vane acb in the figure (α) (front elevation) is turned through an angle θ, as measured by the graduated arc, so as to take up the position ecf, each half of the vane ec or cf creates a sector-shaped shadow in a beam of light in the direction of the arrow; $e'd'$ is a projection of ed. It is shown again in the figure (β) in side elevation, where $e'd'$ is the projection of ed. If the beam of light were rectangular in section, the shadow would be triangular in shape ($e'd'o$) and proportional in area to $\sin\theta$, since ed, which subtends the angle θ, is equal to e_1d_1, which subtends the angle ϕ at the optic axis, O, for ed' and $d'o$ are equal, since they form the right angle in the isosceles triangle $ed'o$; therefore $ed/ed' =$

$e'd'/d'o$, that is, $\sin \theta = \tan \phi$, whence θ being known, ϕ may be found directly from the tables.

The beam of light, however, is circular in section; hence the area of any sector in the circle is proportional to the angle which it contains, that is, to ϕ for the shadow and $45° - \phi$ for the sector aperture.

Only one-eighth of the whole circular aperture has been considered, but it will be seen on cancelling common factors that the whole aperture at any moment is measured by $45° - \phi$, where $45°$ is taken to represent the fully open sector. It is convenient to express the apertures as percentages of the whole aperture, that is, $\dfrac{(45 - \phi)100}{45}$. The percentage apertures and values for $\log I/I'$ corresponding with each half-degree on the graduated arc have been calculated by Miss Gartha Thompson, to whom the author is indebted for valuable assistance throughout the inquiry. Examples are given in the following table:

θ.	Sin θ or tan ϕ.	ϕ.	$45 - \phi$.	Sector aperture, per cent. $\dfrac{(45 - \phi) \, 100}{45}$	Log I/I', $\log \dfrac{45}{45 - \phi}$
10	0·1736482	9·85108	35·14892	78·11	0·1073
25	0·4226183	22·90981	22·09019	49·08	0·3091
40	0·6427876	32·73241	12·26759	27·27	0·5644
40·5	0·6494480	33·00163	11·99837	26·67	0·5740
41	0·6560590	33·27239	11·72760	26·07	0·5839
55	0·8191520	39·32269	5·67731	12·62	0·8991
70	0·9396926	43·21918	1·78082	3·958	1·4026
80	0·9848078	44·56143	0·43857	0·975	2·0111
80·5	0·9862856	44·60441	0·39559	0·870	2·0559
81	0·9876883	44·64512	0·35488	0·789	2·1031
85	0·9961947	44·89078	0·10922	0·243	2·6150
85·5	0·9969173	44·91155	0·08845	0·197	2·7065
88	0·9993908	44·98255	0·01745	0·0388	3·4114

It is evident that the values in the table can be applied to graduating the arc on the instrument so that it may read directly in terms of $\log I/I'$, as has been done with other instruments. This is convenient where it is intended to use the instrument for routine work only, but for versatile research, and especially where it is desired occasionally to elaborate a particular part of an absorption curve, the freedom conferred by the ordinary scale and tables will be appreciated. There is, however, no difficulty in providing both scales on the same arc.

The effect produced by the size of the shadow cast by the vane being a function of the sine of the angle through which the vane has been turned is significant. From the above figures, it will be

seen that the difference in the sector aperture produced by a constant difference of 15° in θ decreases continuously, thus:

Per cent.

Between 10° and 25° the aperture decreases by (78·11—49·08) 29·03
,, 25° ,, 40° ,, ,, ,, ,, (49·08—27·27) 21·81
,, 55° ,, 70° ,, ,, ,, ,, (12·62— 3·96) 8·66
,, 70° ,, 85° ,, ,, ,, ,, (3·96— 0·24) 3·72

Again, for half-degree intervals in θ:

Between 20° and 20·5° the aperture decreases by (58·03—57·09) 0·94
,, 40° ,, 40·5° ,, ,, ,, ,, (27·27—26·67) 0·60
,, 80° ,, 80·5° ,, ,, ,, ,, (0·975—0·879) 0·096
,, 85° ,, 85·5° ,, ,, ,, ,, (0·243—0·197) 0·047

For any of the apertures of small size, it is evident, therefore, that a movement of the pointer on the arc over one or more divisions alters the size of the aperture by only a small fraction, so that any probable error in construction or manipulation can have no detectable effect on the measurement of the size of the aperture.

The possibility of regulating the size of the small apertures with such precision is a valuable advantage, since it is with these that much of the more important and delicate work is done.

In an investigation of uric acid, undertaken to see if it obeyed Lambert's law, it was proved that the results for all the small apertures down to 0·29 per cent. (reading 84·5° on the graduated arc and giving the value 2·53 for $\log I/I'$) harmonised perfectly with those found for the larger apertures. The still smaller ones were not quite so true, owing to a slight imperfection in the setting of the vanes, but this can be avoided in reproducing the instrument.

The instrument is absolute in all its measurements. That it is not only so, but that it is also precise, follows from the examination of a standard piece of glass which was supplied by Messrs. Adam Hilger with their photometer for calibration purposes. The figures obtained are tabulated below. The two sets of values for $\log I/I'$ are as follows: (a) those obtained by the new photometer; (b) the figures given by Hilger:

Wave-length.	(a).	(b).
2751	0·281	0·278
2636	0·665	0·610
2564	0·919	0·888
2478	1·318	1·330
2435	1·605	1·608
2389	1·970	1·940

Of the two methods, the one with the new photometer has the advantage of being direct and of not depending on the assumption

that photometry in the ultra-violet is uniform with that in the visible region and on the use of accessory apparatus, as in the method published by Hilger. In any case, the two series of results are sufficiently similar to one another to call for a discussion as to which is the more accurate expression of the phenomena.

Considerable advantage is gained by having two sectors which are equal in all respects, as in the new photometer. As already stated, the substance can be placed in the first and second paths alternately, so that any slight imperfections in the sectors or in any part of the optical train will express themselves in opposite senses in the two series of spectra; also the work will be confirmed and experimental error corrected at the same time. The mean of the two closely concordant results must be a very near approximation to the truth.

Further, opportunity is provided for eliminating the effect of the solvent directly. Most of the solvents, alcohol, for example, give feeble absorption spectra which spoil the accuracy of the extinction coefficients of the dissolved substance under investigation. It is not altogether satisfactory to correct the absorption constants of the solution by subtracting those due to the solvent, which have been ascertained separately, and in any case it is laborious to do so; for example, it is not safe to assume that a standard curve for absolutely pure alcohol applies to commercially pure spirit. Indeed, some of the impurities commonly occurring in rectified spirit are strongly absorbent of ultra-violet light. It is better to place in the one path a tube of the solution, and in front of the constant sector a similar tube filled with the same solvent as that used in making the solution. It is a good plan to have a tube of the given solvent in each of the two paths when adjusting the instrument, and then to replace the solvent in one of them by the solution in question. It is perhaps unnecessary to do so, but it lends a sense of satisfaction, while it adds little or nothing to the experimental work. It is certain that the differences then observed in the two spectra are due entirely to the substance in the dissolved state, and hence its absorption curve can be derived directly. There is, however, the possibility of the absorption spectrum being modified by the association of the solute with the solvent, but that is a matter for other inquiry in each particular case and does not affect either the general truth of the proposition or the operation of the instrument.

XXXIII.—*The Formation and Stability of* spiro-*Compounds. Part II. Bridged*-spiro-*compounds Derived from* cyclo*H*exane.

By CHRISTOPHER KELK INGOLD and JOCELYN FIELD THORPE.

INTRODUCTION.

(A) *General.*

IN Part I. of this series (Beesley, Ingold, and Thorpe, T., 1915, ·107, 1080) a comparison was drawn between the conditions of formation and the stability of the bromo-esters of $\beta\beta$-dimethylglutaric acid and cyclohexane-1:1-diacetic acid. These two acids contain respectively the structures I and II, and the object with which

$$\begin{array}{c}\text{CH}_3\\\text{CH}_2\end{array}{>}\text{C}{<}\begin{array}{c}\text{C}\\\text{C}\end{array} \qquad \text{CH}_2{<}\begin{array}{c}\text{CH}_2\cdot\text{CH}_2\\\text{CH}_2\cdot\text{CH}_2\end{array}{>}\text{C}{<}\begin{array}{c}\text{C}\\\text{C}\end{array}$$

(I.)   (II.)
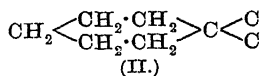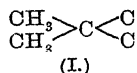
these comparisons were made may be indicated by reference to Figs. (i) and (ii), which are drawn to correspond with structures I and II. The question discussed was whether the forcing apart of the valencies (a) and (b) of a carbon atom from an inclination of $2\tan^{-1}\sqrt{2}$ to one of $\frac{2}{3}\pi$ radians, which, according to Baeyer's strain theory necessarily accompanies the production of the cyclohexane ring, would cause the other two valencies (c) and (d) to approach one another. They might, it was suggested, approach one another in such a way as to divide the remaining space into three equal angles as in Fig. (ii A); or, alternatively, they might be quite unaffected by the straining of (a) and (b) and remain, as Fig. (ii B) shows, at the normal angle of $2\tan^{-1}\sqrt{2}$.

It was pointed out that if the first of these hypotheses, that represented in Fig. (ii A), were correct, and side-chains attached to (c) and (d) were in closer proximity when (a) and (b) were bound in a cyclohexane ring than is the case in Fig. (i), where (a) and (b) are free, then the elimination of groups or elements such as, for example, hydrogen and bromine as hydrogen bromide, from the side-chains of substitution products of cyclohexanediacetic acid should proceed with greater readiness than when corresponding derivatives of dimethylglutaric acid are employed. Further, the ring compounds formed as a result of the elimination might be expected to possess a greater general stability in the former case than in the latter. If, on the other hand, the second alternative,

for which Fig. (ii B) is drawn, is the correct one, there should be no difference in the two cases.

Experimental evidence was, as a matter of fact, clearly in favour of the first hypothesis. Thus, for example, *trans-cyclo*hexane*spirocyclo*propane-1 : 2-dicarboxylic acid, which contains the carbon

Fig.(i)
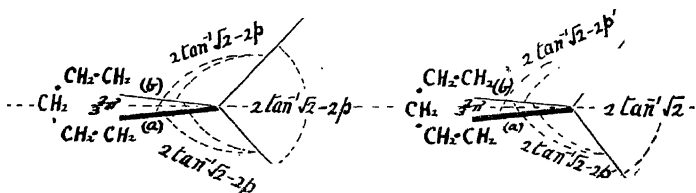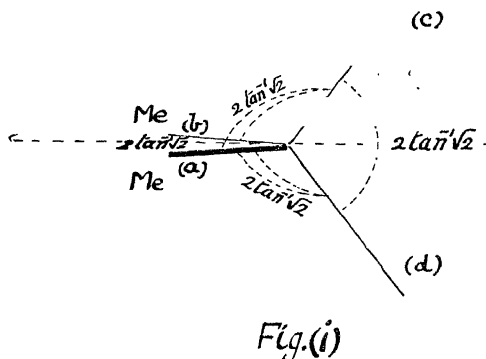
skeleton IV, was found to possess a distinctly greater stability than *trans*-caronic acid represented by the outline III :

$$CH_3 \atop CH_3 \Big\rangle C \Big\langle {C_{(1)} \atop C_{(2)}}$$
(III.)

$$CH_2 \Big\langle {CH_2 \cdot CH_2 \atop CH_2 \cdot CH_2} \Big\rangle C \Big\langle {C_{(1)} \atop C_{(2)}}$$
(IV.)
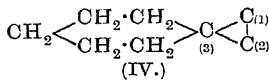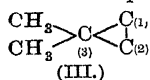
The present paper extends the comparison to substances of a rather more complex type, which contain a *cyclo*butane ring joined to the

*cyclo*propane ring by two carbon atoms common to both. The structures of these compounds are indicated by the outlines V and VI:

$$CH_3 \!\! > \!\! C \!\! < \!\! \begin{matrix} C\!-\!C_{(2)} \\ | \quad | \\ C\!-\!C_{(3)} \end{matrix} \qquad CH_2 \!\! < \!\! \begin{matrix} CH_2 \!\cdot\! CH_2 \\ CH_2 \!\cdot\! CH_2 \end{matrix} \!\! >_{(5)} \!\! C \!\! < \!\! \begin{matrix} \overset{(1)}{C}\!-\!C_{(2)} \\ | \quad | \\ \underset{(4)}{C}\!-\!C_{(3)} \end{matrix}$$

$$\text{(V.)} \qquad\qquad\qquad \text{(VI.)}$$
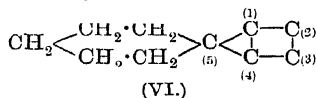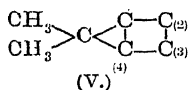
It is apparent that the presence of the *cyclo*butane ring in structures V and VI will make a considerable difference in the kind of effect that one might expect to observe. This can best be understood by representing the strained valencies according to a graphical method which depends for its rational basis on the following considerations.

In Fig. (iii), which is drawn to correspond with formula III, the

Fig. (iii)
(*Cyclo*propane ring in plane of paper.)

Fig. (iv)
(*Cyclo*propane ring in plane of paper.)

Fig. (v)
(*Cyclo*propane ring in plane of paper.
*Cyclo*butane ring inclined to paper.)

Fig. (vi)
(*Cyclo*propane ring in plane of paper.
*Cyclo*butane ring inclined to paper.)
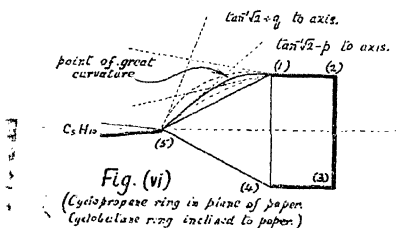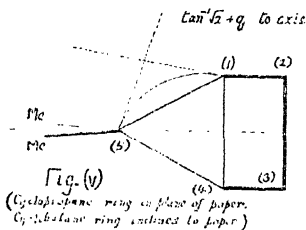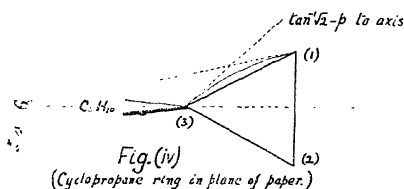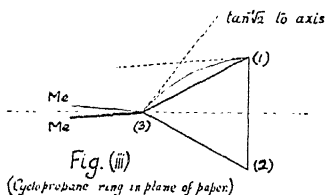
carbon atoms of the *cyclo*propane ring are represented as points at the corners of an equilateral triangle. Now in the case of such a compound as ethane it can scarcely be doubted that the resultant of the attracting forces which bind the two carbon atoms together, that is to say the valency, is directed along the straight line joining the centres of the carbon atoms. With *cyclo*propane, however, the case is different. For here, according to the strain theory, we have each one of the carbon atoms of the ring reacting on those of its valencies which participate in the ring in such a way as to *tend* to make them emanate from the atom in directions inclined to one another at an angle of $2 \tan^{-1}\sqrt{2}$. If the carbon atoms were entirely successful in bringing about this result, then, since two

valencies emanating from the same carbon atom at an angle of $2 \tan^{-1}\sqrt{2}$ have to reach the two remaining corners of the equilateral triangle, it is clear that the only way in which they could do so is by describing curved paths. The simplest curve which, in these circumstances, a valency could describe would be the arc of a circle each of the terminal tangents of which makes an angle of $\tan^{-1}\sqrt{2}$ with the median through the corresponding corner of the equilateral triangle. This path is drawn in the case of the valency (3 : 1) in Fig. (iii). It represents a state in which the carbon atoms would be entirely free from distortion of the kind we are considering, the whole being borne by the valencies; that is to say, the physical stress would reside solely on the inter-atomic medium in which the forces of valency are propagated. The valencies will, however, on their part, tend to reduce their potential energy by shortening their paths, and if *they* completely succeeded would stretch themselves along the straight lines joining the carbon atoms. This would throw the whole of the strain back on the latter, since now the initial directions in which the ring-valencies leave a carbon atom are inclined, not at $2 \tan^{-1}\sqrt{2}$, but at $\pi/3$. It is probable, therefore, that an equilibrium of stresses will be set up, and that the valencies will occupy paths which lie between the straight lines and the limiting arcs, the arrangement being of such a kind as to cause part of the strain to be taken up by the distorted carbon atoms and part by the bent valencies.

Experimental support can be claimed for this view. For in Part I. there were recorded experiments which yielded decided evidence that part at least of this kind of strain is actually taken up by the carbon atoms. In particular, it was shown that, when two valencies of a carbon atom are bound in a *cyclo*hexane ring, groups attached to the other two valencies apparently take up an altered relative position. It is obvious that this could never happen if the strains existing in the *cyclo*hexane ring resided solely on the valencies participating in the ring, none at all being borne by the carbon atom which carries the side-chains. Similarly, strains existing in one ring of a *spiro*-compound could not possibly make themselves felt in the second ring unless communicated by a spirane carbon atom, which itself is in a state of strain. According to the experiments described in Part I., such communication of strain across the spirane carbon atom appears actually to take place, and one can only conclude therefrom that the spirane atom itself is by no means in an unstrained condition.

If it be true that part at least of the strain of the *cyclo*hexane ring is actually taken up by the carbon atoms, then regarding the matter from the graphical point of view, we may say that the

valencies of the *cyclo*hexane ring, and presumably of any other alicyclic ring, occupy paths which are distinctly flatter than the limiting arcs the terminal tangents of which meet at the normal angle $2 \tan^{-1} \sqrt{2}$.

On the other hand, it will be shown in the present paper that it is more difficult to close the *cyclo*butane ring in the formation of certain bridged-*spiro*-compounds of the type VI (p. 322) than it is in the formation of corresponding bridged-ring compounds of the type V (p. 322). Further, the former, when obtained, are less stable than the latter in certain specific positions entirely in accord with the views here put forward. If the stresses existing in the *cyclo*hexane ring can be communicated to the *cyclo*butane ring, or to side-chains attached to the *cyclo*propane ring before the *cyclo*-butane has been closed, then it follows that the valencies of the *cyclo*propane ring, as well as the spirane carbon atom, must take part in the transmission of stress. With entirely unstrained valencies this is inconceivable, and one is therefore forced to the conclusion that the valencies themselves are strained.

The graphical aspect of this is that the valencies concerned, and therefore probably all ring-bound valencies, must occupy paths which are not straight lines, which are, in fact, distinctly curved. The curvature of such a path will, as we have already seen, be less than that of the limiting arc the terminal tangents of which meet at $2 \tan^{-1} \sqrt{2}$, and the path may therefore be regarded as lying somewhere between a straight line on the one hand and a limiting curve on the other.

Exactly where the position of equilibrium of a particular valency lies, and what the precise shape of its true path is, it is impossible at present to say; but the view that the true equilibrium-path lies somewhere between the rectilinear path, which represents the limiting case in which the valency is unstrained, and the curved path which stands for the other limit in which the whole of the distortion resides on the valency and none at all on the carbon atom, affords a simple, and, so far as it goes, a fairly adequate hypothesis in regard to the facts observed. If we accept the point of view that the more strained a valency is the more prone it is to break, then among the factors which determine the equilibrium of strain-distribution will certainly be found the number of groups attached to the carbon atoms concerned; for the tendency which ring compounds have to undergo fission between quaternary carbon atoms is well known. The electrochemical character of the substituents will, of course, be another determining factor.

Thus it would seem that there are three causes affecting the

stability of any valency which participates in a fully reduced alicyclic structure:

(1) The number of carbon atoms in the ring,

(2) The character and mode of attachment of any attached rings, and

(3) The number, distribution, and character of the substituent groups.

In regard to the first of these causes Baeyer's simple conception has had a very great degree of success in explaining the broad facts; so much so that one cannot but accept it as an approximation to the truth. In its elemental form, however, it does not consider the question as to whether the atoms or the valencies are the seat of the postulated strain, and, consequently, is not in a position to take into account the mode of operation of causes (2) and (3), which present us with two unsolved problems. The series of which this paper is Part II. is an attack on the former of these. In regard to the latter all that can at the moment be said is that the present considerations lead to the view that whilst causes (1) and (2) determine the maximal strain or curvature which any particular valency can be called on to bear, cause (3) operates in such a way as to settle exactly what fraction of that maximum it shall bear.

The uncertainty which surrounds the operation of cause (3) constitutes a difficulty which one meets with in planning experiments with a view to study the mode of action of cause (2). If, however, one is careful only to compare substances in which similar, and similarly situated, substituent groups are present, the strain on a valency may fairly be taken to be measured by the greatest strain which that valency could be called on to bear in the limiting equilibrium. It will actually, of course, be just a fraction of this, but if the groups are alike it will be the same fraction for all the substances. In such cases, therefore, the strain existing on a valency is, from the graphical point of view, measured by the degree of curvature of the limiting curved path.

Fig. (iii), p. 322, is an application of this method to the *cyclo*-propane ring structure III (p. 321), and has already been mentioned. The limiting curve for the valency (3:1) is drawn. Its terminal tangents make angles of $\tan^{-1}\sqrt{2}$ with the corresponding medians, and its curvature, taking the side of the triangle as unity, is $\sqrt{2} - \tfrac{1}{3}\sqrt{3}$.

Applying the same method to the *cyclo*hexane-*spirocyclo*propane structure IV (p. 321) we obtain Fig. (iv) (p. 322), in which, for reasons referred to at the beginning of this paper and given in detail in Part I., the terminal tangents of the limiting curve of the

valency (3:1) are drawn to make angles with the corresponding medians less than the normal value $\tan^{-1}\sqrt{2}$ by, say, p radians. The curvature of this curve is less than that of the curve in Fig. (iii) by about $\frac{1}{6}(7-2\sqrt{6})p$, a figure which may be taken as a measure of the increase in stability of the bond (3:1) which was proved experimentally in Part I.

The structure V (p. 322) is interesting as exhibiting a difference in exactly the opposite sense. The fact that two of the valencies of the carbon atom (1) are held in a *cyclo*butane ring will, according to the views put forward in Part I., tend to make the initial directions in which the other two valencies leave the carbon atom spread out in such a way as to form angles with one another and with the *cyclo*butane-ring-bound valencies greater than would be the case if the *cyclo*butane ring had not been closed. This will involve an increase in the initial divergence of the valencies (1:4) and (1:5). The limiting arc between the carbon atoms (5) and (1) is therefore drawn (Fig. v, p. 322) to suit terminal tangents inclined to the corresponding medians at angles which are greater than $\tan^{-1}\sqrt{2}$ by, say, q radians. The curvature is therefore greater than $\sqrt{2}-\frac{1}{3}\sqrt{3}$ by about $\frac{1}{6}(7-2\sqrt{6})q$.

The point of present interest is, of course, to see how a bridged-ring compound of the type V compares with a bridged-*spiro*-compound of the type VI (p. 322). It will be observed that in the latter case the limiting curve for the valency (5:1) cannot possibly be symmetrical. For whilst the carbon atom (5) is, on account of the *cyclo*hexane ring, tending to reduce the angle which the terminal direction of the curve makes with the median to the value $\tan^{-1}\sqrt{2}-p$ radians, the carbon atom (1), as a result of its being involved in the *cyclo*butane ring, is endeavouring to enhance the corresponding angle at that end of the curve to $\tan^{-1}\sqrt{2}+q$ radians. The true curve, therefore, will lie between the dotted arcs of curvatures $\sqrt{2}-\frac{1}{3}\sqrt{3}-p/6(7-2\sqrt{6})$ and

$$\sqrt{2}-\frac{1}{3}\sqrt{3}+q/6(7-2\sqrt{6}),$$

approximating to the inner arc near the carbon atom (5), and to the outer near the carbon atom (1). Such a path, it is clear from Fig. (vi) (p. 322), must contain a region of comparatively great curvature, and we may therefore expect the bond (5:1) in bridged-*spiro*-compounds of the type VI (p. 322) to be noticeably less stable than the same bond in corresponding compounds of the bridged-ring series V.

The effect just noticed will, of course, be by far the greatest which the *cyclo*hexane ring could be expected to have on the attached dicyclic system. The reactions on the bonds (1:2) and (1:4) will

be next in importance, but of the second order. It is, however, of interest briefly to examine them. The fact that the limiting curve of the valency (5 : 1) is, on the whole, depressed below the arc which corresponds with the limiting curve of the same valency in Fig. (v) necessitates that the true path of the same valency in Fig. (vi) is, even near the carbon atom (1), rather less divergent from the rectilinear path than is the case in Fig. (v). This will involve a small effect on the valency (1 : 2) in the direction of an increase in the curvature of its limiting curve. The bond (1 : 2) should therefore be slightly more strained and less stable in the series VI than in the series V.

The effect of the strains in the *cyclo*hexane ring on the bridge-bond (1 : 4) is also of the second order, the depression of the bond (5 : 1) being the determining factor. In this case the fact that the bonds (1 : 5), (1 : 4), and (1 : 2) have their curves in different planes makes the geometrical construction more complicated. It would appear, however, that the effect should be in the direction of a decrease of stability, although, of course, a very slight one.

There remains for consideration the bond (2 : 3). The effect in this case will be still smaller, of the third order in fact, and probably beyond the limits of detection. It should be in the direction of an increase in stability.

It may be stated here that the results of the experiments described in this paper are in the most complete accord with all the above conclusions.

The most striking fact which emerged during the experimental study was the marked decrease in the stability of the bond (5 : 1), of compounds of the type VI, when compared with corresponding substances of the type V (see sections C, D, and G). The fission of this bond was brought about with great ease in certain substances of the former type by alkaline reagents which appeared to be without effect on the latter. This is in agreement with the first of the main conclusions reached as a result of the conception of flexible valencies. The agreement is particularly interesting in this case, for whereas in the comparison of the *cyclo*propane derivatives of types III and IV (p. 321) carried out in Part I. it was found, in agreement with the requirements of theory, that the *cyclo*hexane ring had a stabilising influence, in the bridged series V and VI the hypothesis leads us to anticipate exactly the reverse.

Definite experimental evidence (section B) was also obtained on the effect on the bond (1 : 2) of the presence of the *cyclo*hexane ring in the *spiro*-compounds. The expected effect is in the nature of an increase in strain, that is, a decrease in stability, and is small in magnitude. Actually we were not able to find a reagent which

would break this bond in a compound of the type VI (p. 322), and would not also break the same bond in one of the type V. This was, at any rate, in part, due to the fact that it did not appear to be possible to break the bond (1:2) in the series VI without first breaking the less stable bond (5:1). This, so far as it goes, is valuable, as it indicates that the effect of the *cyclo*hexane ring on the bond (1:2) is of a smaller order than the effect on the bond (5:1). Fortunately, there is, however, a more precise and more delicate method of experiment. The *cyclo*hexane*spiro*dicyclopentane structure VI was, in our experiments obtained from *cyclo*hexane-1:1-diacetic acid by a method which involved first the closing of the *cyclo*propane ring, and then of the *cyclo*butane ring, by the establishment of the bond (3:4). Now the additional instability which we have been led to expect the bond (1:2) in the *spiro*-structure VI to exhibit is due to the tendency which there is, owing to the *cyclo*hexane ring, for the angle between the bonds (1:4) and (1:5) to increase. It is obvious that this tendency will have greater effect if the bond (3:4) has not been established than would be the case if it had, for in the former case the tendency will not be resisted by the strained bonds of the *cyclo*butane ring. The result will be to magnify the effect by drawing further apart the carbon atoms (3) and (4) to an extent which might quite well be sufficiently great to make it appreciably more difficult to close the *cyclo*butane ring in the series VI than in the series V. A set of comparative experiments, made in order to discover whether such an effect could be detected, revealed its existence very clearly. The interest of these experiments lies in the fact that they show that the stresses in the *cyclo*hexane ring have been communicated to the bond (1:2), a phenomenon which would seem necessarily to involve the assumption that the bond (5:1), as well as the carbon atoms (5) and (1), are in a state of strain.

With regard to the bond (1:4) in the structures V and VI (p. 322) there is available quite a good method of experiment, since sodium amalgam readily breaks this bond in certain substances belonging to these types without attacking in the slightest degree any of the other bonds in the molecules (see section E). The reductions occupy several hours, and can readily be conducted at constant temperature and under comparable conditions. By making comparative experiments along these lines it was discovered that, although the reactions proceeded in much the same way in the two cases, there was a considerable difference in the reaction velocities, the reductions proceeding more rapidly in the bridged-*spiro*-series VI than in the bridged-ring-series V. This is in agreement with the conclusions already reached on theoretical grounds (p. 327), but it

has also some interest from another point of view. It might be thought possible that valencies are so extremely elastic as to be capable of stretching as well as of bending. If that be so, the valency (1:4) ought to be less stretched out in the structure VI, in which the *cyclo*hexane ring is tending to reduce the angle at which the bonds (5:1) and (5:4) emerge from the spirane carbon atom (5), than in the structure V, which contains no *cyclo*hexane ring. Any such difference in the degree of elongation of the bond (1:4) ought to manifest itself as a marked difference of stability, since the forces between two carbon atoms must vary as some power, probably a high power, of the distance between them. As a matter of fact, the difference of stability which the reduction experiments reveal is in precisely the opposite sense from that which this view requires. This appears to us to show that no appreciable lengthening occurs, and that probably all carbon-to-carbon valencies have the same fixed length. It may also be noticed that the effect observed is the opposite to what would be expected if the bonds occupied inflexible straight lines. For in this case the tendency which the *cyclo*hexane ring has to reduce the angle between the bonds (5:1) and (5:4) (compare Part I.) should operate in such a way as to increase the stability of the bond (1:4). These facts, therefore, constitute a strong argument in support of the conception of flexible valencies.

There remains to be mentioned finally a set of experiments which were undertaken in order to obtain information regarding the bond (2:3). This bond, according to the conclusions expressed on p. 327, should be practically unaffected by the strains in the *cyclo*hexane ring. Actually we were not successful in finding a reagent which would attack this bond in a compound of the type VI, even when the stability of the bond was reduced by the introduction of an alkyl group at the carbon atom (2), without first attacking one of the *cyclo*propane bonds adjacent to the spirane carbon atom. However, the experiments were interesting as confirming our previous experiences regarding the instability of these bonds, and were in harmony with the conclusions already reached in regard to the insignificance of the effect which the *cyclo*hexane should have on the bond (2:3).

In order to avoid confusion in what follows it ought perhaps to be pointed out that the bonds (5:1) and (5:4) are equivalent in the carbon skeletons V and VI (p. 322), and only become dissimilar when substituent groups are introduced unsymmetrically. This is actually the case with the compounds with which we have experimented, and it so happens that the bond split in all the substances which were subjected to fission by alkalis is, according to the method

of numbering employed throughout, the bond (5 : 4), not the bond (5 : 1). This, it is clear, invalidates nothing, and, in fact, the agreement would be formal as well as actual if in the formulæ which follow we had numbered the di*cyclo*pentane ring the other way round. The objection to doing this is that one would then meet with the same lack of formal consistency in regard to the bonds (1 : 2) and (3 : 4).

(B) *Formation of the Bridged-ring Systems V and VI* (p. 322): *Closing of the* cyclo*Butane Bond* (3 : 4).

Some time ago, in a paper published by one of us in conjunction with W. H. Perkin (T., 1901, **79**, 729), it was shown that when the dibromo-ester of $\beta\beta$-dimethylglutaric acid (VII) was treated with ethyl malonate and sodium ethoxide, condensation took place in two stages, the ultimate product being an insoluble, yellow sodium derivative of ethyl dimethyldi*cyclo*pentanonetricarboxylate (IX). It was

$$\mathrm{CH_3{>}C{<}^{CHBr\cdot CO_2Et}_{CHBr\cdot CO_2Et}} \xrightarrow[\text{malonate}]{\text{ethyl sodio-}} \mathrm{CH_3{>}C{<}^{C(CO_2Et)\cdot CH(CO_2Et)_2}_{CH\cdot CO_2Et}}$$

(VII.)   (VIII.)

$$\mathrm{CH_3{>}C{<}^{\overset{(1)}{C}(CO_2Et)\cdot C{:}C(ONa)\cdot OEt}_{\underset{(4)}{C}(CO_2Et)\cdot \overset{(2)}{C}O_{(3)}}}$$

(IX.)
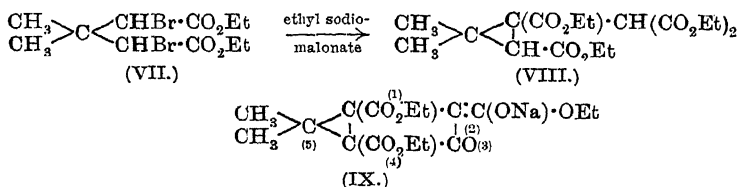
therefore to be expected that if *cyclo*hexane-1 : 1-diacetic acid were used in place of dimethylglutaric acid a similar condensation would ensue:

$$\mathrm{CH_2{<}^{CH_2\cdot CH_2}_{CH_2\cdot CH_2}{>}C{<}^{CHBr\cdot CO_2Et}_{CHBr\cdot CO_2Et}} \xrightarrow[\text{malonate}]{\text{ethyl sodio-}}$$

(X.)

$$\mathrm{CH_2{<}^{CH_2\cdot CH_2}_{CH_2\cdot CH_2}{>}C{<}^{C(CO_2Et)\cdot CH(CO_2Et)}_{CH\cdot CO_2Et}} \xrightarrow[\text{ethoxide}]{\text{sodium}}$$

(XI.)

$$\mathrm{CH_2{<}^{CH_2\cdot CH_2}_{CH_2\cdot CH_2}{>}\overset{(1)}{\underset{(5)}{C}}{<}^{C(CO_2Et)\cdot C{:}C(ONa)\cdot OEt}_{C(CO_2Et)\cdot CO_{(3)}}}$$

(XII.)
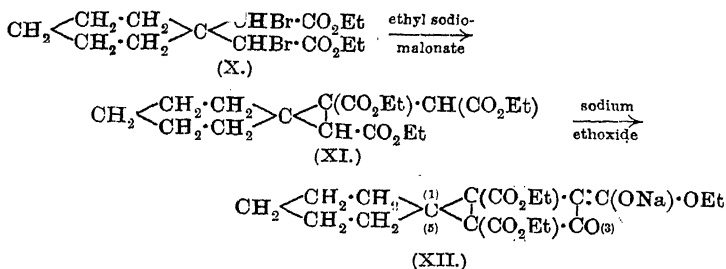
The sodium derivatives IX and XII clearly belong respectively to the types V and VI (p. 322), and it was therefore decided to make their formation and decompositions subjects of comparison.

It was found possible to prepare the sodium *spiro*-compound (XII) direct from ethyl dibromo*cyclo*hexanediacetate (X) and ethyl

sodiomalonate under the same conditions as are employed in pre-
paring the sodium ring compound (IX) from ethyl dibromodi-
methylglutarate (VII).   Direct comparison of the two condensations
is, however, complicated by the fact that, whilst ethyl dibromo-
dimethylglutarate (VII) can readily be obtained in a state of purity
by distillation, the corresponding *cyclo*hexane derivative (X) decom-
poses when distilled.   We were therefore forced to use a crude
bromination product containing only 76—80 per cent. of the
dibromo-ester.   Nevertheless, the difference between the two cases
is significant.   Two experiments, one with the bromo-ester of
dimethylglutaric acid, and the other with the bromo-ester of *cyclo*-
hexanediacetic acid, carried out under comparable conditions
(except that sufficient excess of the crude *cyclo*hexane ester to allow
for the impurities was used); gave in the first case a 62 per cent.
yield of the sodium compound (IX, p. 330), and in the second a
13 per cent. yield of the sodium *spiro*-compound (XII, p. 330).

In order to make the comparison more definite, the tetraethyl
ester XI (p. 330) was prepared in a state of purity.   The internal
condensations of the esters VIII and XI (p. 330) with alco-
holic sodium ethoxide, whereby alcohol is eliminated and the
bridged structure formed, were then carried out in a series of
experiments made under comparable conditions.   Several pairs of
parallel experiments were made, in which the two esters were boiled
with alcoholic sodium ethoxide under standard conditions for dif-
ferent lengths of time, at the end of which the insoluble sodium
compounds were collected and weighed.   The results are given in
the experimental part of this paper (p. 359).   The figures for the
yields in the two cases lie upon fairly smooth but widely divergent
curves (Fig. vii).   These curves clearly show that the velocity of
formation of the bridged-ring structure is much greater than the
velocity of formation of the *spiro*-compound.   The times required
for a 20 per cent. conversion are in the ratio of approximately
10 to 1.   An examination of the curves shows that, if x is the yield
(per cent.) and t the time, the quantity $- \partial/\partial x(dx/dt)$ is almost
invariable with time and has a definite positive value for each curve,
being about $0 \cdot 97^{-1}$ hours for the bridged-ring compound and about
$0 \cdot 33^{-1}$ hour for the bridged-*spiro*-derivative.   The velocity constants
for the formation of the sodium compounds are therefore approxi-
mately in the ratio of 3 to 1.   The best yields obtainable in the two
cases are 77 per cent. and 38 per cent. respectively, but a longer
time is necessary to produce a 38 per cent. yield of the *spiro*-com-
pound than is required to obtain a 77 per cent. yield of the ring
compound.   The fact appears to be that the *spiro*-ester XI (p. 330)
will only condense with itself when present in the sodium ethoxide

in considerable concentration.   For, whereas under the experimental conditions which give the best yield (77 per cent.) of the sodio-ester, IX, the tetraethyl ester, VIII (p. 330), almost entirely disappears from the reaction mixture, when the ester XI is treated so as to produce a maximal yield of the sodio-*spiro*-ester (38 per cent.), then,

<p style="text-align:center">FIG. (vii).</p>

<p style="text-align:center">Establishment of the bond 3 : 4.</p>
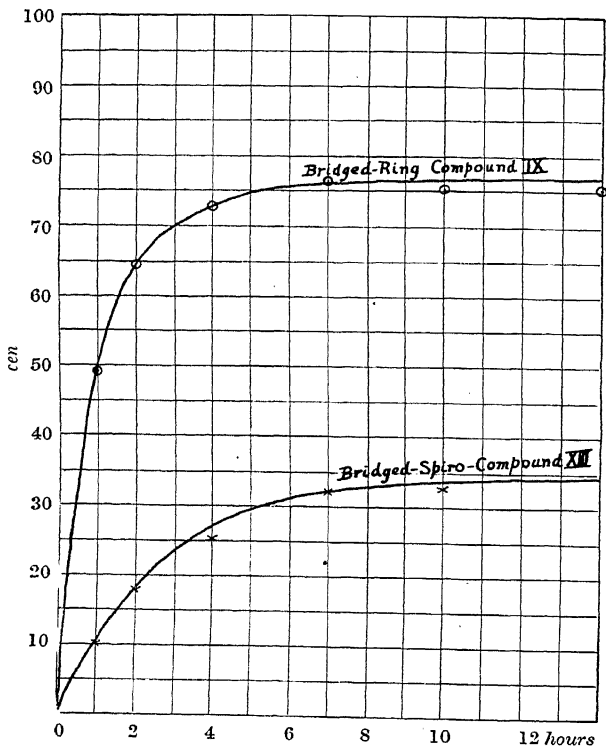
although longer time is allowed in this case, the conversion is found to be only partial, about 15 per cent. of the tetraethyl ester being recoverable.   Yet prolonging the time of reaction does not appear appreciably to increase the yield of sodium compound or reduce the quantity of tetraethyl ester recovered.

Tbese experiments clearly show that it is more difficult to estab-

lish the bond (3:4) of the *cyclo*butane ring to form the *spiro*-compound XII than it is in the formation of the ring compound IX. Indeed, the low yield of the former compound was one of the greatest practical difficulties of the research.

(C) *Hydrolytic Decompositions of the Bridged-Ring Derivatives IX and XII* (p. 330): *Stability of the* cyclo*Propane Bond* (4:5).

The first evidence of a difference of stability between compounds of the bridged-*spiro*-series VI and those of the bridged-ring series V (p. 322) was obtained in the course of some experiments on the hydrolysis of the sodium *spiro*-compound XII (p. 330).

The effect of hydrolysing agents on the sodium compound IX has already been described in the paper with W. H. Perkin (*loc. cit.*), and the general conclusion reached was that the end-product of the action of alcoholic potassium hydroxide was a mixture of the dibasic and monobasic acids XIII and XIV, and that the same two acids

$$CMe_2 < {}^{\backprime}(CO_2H) \cdot CH \cdot CO_2H$$
$$\text{(XIII.)}$$

$$CMe_2 < {C(CO_2H) \cdot CH_2 \atop CH - - - - CO}$$
$$\text{(XIV.)}$$
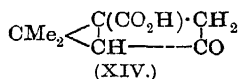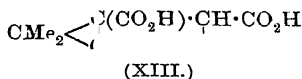
were formed by the action of dilute sulphuric acid. The dibasic acid XIII when heated with water in a sealed tube was found to yield the monobasic acid XIV.

On experimenting along these lines with the yellow sodium *spiro*-compound XII (p. 330) it soon became apparent that the *spiro*-compounds were behaving very differently; the hydrolytic products were therefore investigated in some detail.

When the yellow sodium *spiro*-compound XII was treated with cold dilute acid a colourless, solid ester, $C_{19}H_{26}O_7$ (XV), was pro-

$$C_5H_{10} : C < {C(CO_2Et) \cdot CH \cdot CO_2Et \atop C(CO_2Et) \cdot CO}$$
$$\text{(XV.)}$$
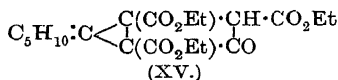
duced. This ester could be transformed by cold alcoholic potassium hydroxide into the yellow potassium salt, XVI, and thence by acids into the colourless acid-ester, XVII.

$$C_5H_{10} : C < {}^{\backprime}(CO_2K) - C : C(OK) \cdot OEt \atop \smash{)}(CO_2Et) \cdot CO}$$
$$\text{(XVI.)}$$

$$C_5H_{10} : C < {C(CO_2H) - CH \cdot CO_2Et \atop C(CO_2Et) \cdot CO}$$
$$\text{(XVII.)}$$
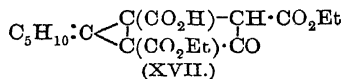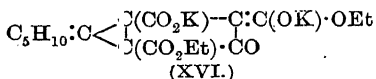
Regarding the question as to which of the three carbethoxyl groups has been attacked by the reagent, it is clear that it cannot be that attached to the carbon atom (2); for if it were, the forma-

tion of a yellow, insoluble potassio-compound so very similar to the original sodium compound would be exceedingly improbable. The fact that it is the 1-carbethoxyl group, and not the 4-carbethoxyl, which has been attacked follows from the production by further hydrolysis of the acid-esters XVIII and XXI, about the constitution of which no doubt exists.

The first product of the action of boiling alcoholic potassium hydroxide on either of the compounds XVI or XVII was a colourless, very readily soluble potassium salt of the ethyl dihydrogen ester XVIII:

$$C_5H_{10}\!:\!C\!\!<\!\!{}^{C(CO_2H)-CH\cdot CO_2H}_{C(CO_2Et)\cdot CO}$$
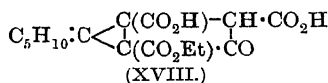
$$(XVIII.)$$

The constitution of the acid-ester XVIII follows from the fact that it is obviously formed by the hydrolysis of the metal-substituted carbethoxyl group in the yellow potassium compound of the diethyl hydrogen ester. The other possible formula (XIX) of the diethyl hydrogen ester would give an ethyl dihydrogen ester of the constitution XX. The formula XX was, however, easily shown to

$$C_5H_{10}\!:\!C\!\!<\!\!{}^{C(CO_2Et)\cdot CH\cdot CO_2Et}_{C(CO_2H)-CO} \qquad C_5H_{10}\!:\!C\!\!<\!\!{}^{C(CO_2Et)\cdot CH\cdot CO_2H}_{C(CO_2H)-CO}$$

$$(XIX.) \qquad\qquad (XX.)$$
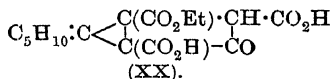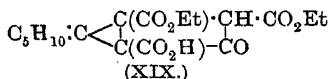
be incorrect by an experiment on the effect of treating the substance with acetyl chloride. With this reagent it readily yielded an anhydride, which, on treatment with water, furnished the original acid-ester. These facts clearly favour formula XVIII, in which the free carboxyl groups are attached to contiguous carbon atoms, and rules out the alternative formula XX. We must also regard XVII as the true formula of the diethyl hydrogen ester, since a substance of the formula XIX could not possibly yield the ethyl dihydrogen ester XVIII.

The acid-ester XVIII can also be produced from the triethyl ester XV (p. 333) by hydrolysis with hydrochloric acid. Indeed, up to this point hydrolysis with alcoholic potassium hydroxide and with hydrochloric acid proceeds along the same lines. The first product of the action of boiling hydrochloric acid on the ester XV is the diethyl hydrogen ester XVII (p. 333), which, by continued action of the same reagent, is converted into the ethyl dihydrogen ester XVIII (above).

The further action of hydrochloric acid causes the substance to decompose simultaneously in two ways, losing, in the one case, a carboxyl group, and in the other a carbethoxyl group. The groups eliminated will, of course, be those in the positions (2) and (4) con-

tiguous to the carbonyl group, and the products must therefore possess the constitutions XXI and XXII:

$$C_5H_{10}\!:\!C\!<\!\!\begin{array}{c}C(CO_2H)-CH_2\\C(CO_2Et)\cdot CO\end{array} \qquad C_5H_{10}\!:\!C\!<\!\!\begin{array}{c}C(CO_2H)\cdot CH\cdot CO_2H\\ \underset{\rule{0pt}{0pt}}{CH}\!\!-\!\!-\!\!-\!\!CO\end{array}$$

$$\text{(XXI.)} \qquad\qquad\qquad \text{(XXII.)}$$
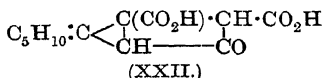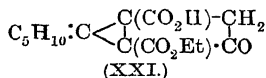
These formulæ are in complete accord with the properties of the substances. The acid-ester XXI, for example, melted without decomposition and gave no coloration with ferric chloride, showing that the free carboxyl group is not adjacent to the carbonyl group, and that the carboxyl group which was attached to the carbon atom (2) in the acid-ester XVIII has been removed. The dibasic acid XXII, on the other hand, melted with decomposition, gave a crimson colour with ferric chloride, and when treated with acetyl chloride gave an anhydride from which the original acid could be regenerated by treating with water. These facts clearly establish formula XXII.

The formation side by side of the acids XXI and XXII does not constitute quite the final stage of the hydrolysis by hydrochloric acid of the ethyl dihydrogen ester XVIII (p. 334). For the acid-ester XXI on prolonged boiling with hydrochloric acid loses its 4-carbethoxyl group, yielding the monocarboxylic acid, XXIII:

$$C_5H_{10}\!:\!C\!<\!\!\begin{array}{c}C(CO_2H)\cdot CH_2\\ \underset{\rule{0pt}{0pt}}{CH}\!\!-\!\!-\!\!-\!\!CO\end{array}$$

$$\text{(XXIII.)}$$
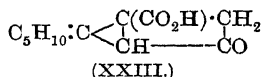
The dibasic acid XXII, on the other hand, was not changed appreciably even on boiling for eighty-seven hours with hydrochloric acid. The final product of the action of this reagent on the acid-ester XVIII was therefore a mixture of the dibasic acid and the monobasic acid (XXII and XXIII).

Further, the dibasic acid XXII was readily converted into the monobasic acid XXIII by heating for a few minutes at 200° with water. All the acid-esters (XVII, XVIII, and XXI) of the series reacted at this temperature with water, giving the same monobasic acid, usually in very good yield. The neutral triethyl ester XV (p. 333), however, required the presence of a trace of an acid, such as acetic or hydrochloric acid, in the water. The presence of a small quantity of butyric acid even was found to be quite sufficient, so that in the cases of the acid-esters the reaction is in all probability autocatalytic, the catalyst being the hydrogen ions produced initially by the electrolytic dissociation of the acid-esters themselves, and in the later stages of the reaction by the dissociation of the monocarboxylic acid XXIII or of carbonic acid. In the case of the

triethyl ester it is necessary artificially to introduce some hydrogen ions in order to start the reaction.

Alkaline hydrolysis of the acid-ester XVIII (p. 334) proceeded in quite a different direction, the product being an acid of the formula $C_{12}H_{16}O_6$. This substance is a dibasic acid. It is not an aldehyde, and contains no lactone ring. It is therefore a fission product formed by the breaking of one of the bonds $(1:2)$, $(1:4)$, $(1:5)$, or $(4:5)$ of the dicyclic system:

$$\overset{(5)}{C}\underset{(4)}{\overset{(1)}{C}(CO_2H)}\overset{(2)}{-CH-CO_2H} \\ C(CO_2H)-CO_{(3)}$$
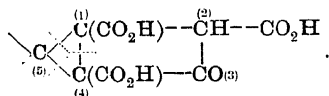
One of the three carboxyl groups originally present in the molecule has been lost, and, since the substance gives no colour reaction with ferric chloride, it is to be presumed that it is the carboxyl group attached to the carbon atom (2) which has disappeared. The question as to which of the four possible bonds has been broken is settled very clearly by the properties of the substance. Thus fission of the *cyclo*butane ring at the bond $(1:2)$ should yield either a derivative containing an open-chain acetoacetic acid residue or a hydroxy-compound capable of forming a γ-lactone, according to the way in which the elements of water are added to the molecule at the point of fission. The substance actually obtained was found to be remarkably stable towards boiling alkalis and showed no tendency to pass into a lactone. On the other hand, although a *trans*-acid, it forms an anhydride with the greatest ease. For this reason it may be safely assumed that the 1- and the 4-carboxyl groups are attached to contiguous carbon atoms, and that the bridge-bond $(1:4)$ has remained intact. The bond which has been broken is therefore one of the *cyclo*propane bonds $(1:5)$ and $(4:5)$, and since the substance is not a γ-hydroxy-acid, it must have one of the two following formulæ:

$$CO_2H \\ C_5H_{10}:CH\cdot C \underset{C(OH)}{\overset{-CH_2-}{<}} >CO \\ CO_2H \\ (XXIV.)$$

$$CO_2H \\ C_5H_{10}:CH\cdot C \underset{-CO-}{\overset{C(OH)}{<}} >CH_2 \\ CO_2H \\ (XXV.)$$
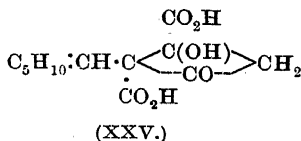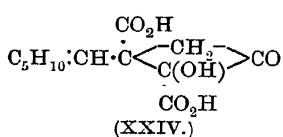
Although both these formulæ are in harmony with the properties of the substance, there can be little doubt that formula XXIV, and not formula XXV, is correct for this reason: The monobasic acid XXIII (p. 335) does not undergo fission with alcoholic potassium hydroxide. The fission therefore seems to be connected with the

quaternary carbon atom in the position (4). If this be so it is reasonable to assume that splitting takes place at a point adjacent to this carbon atom. An indirect but interesting confirmation of this conclusion will subsequently be referred to (p. 345).

The substance to which the formula XXIV has been assigned separates from water with two molecules of water of crystallisation. The anhydrous compound when heated at 250° was found to pass into an anhydride which gave with water a new dibasic acid, also of the composition $C_{12}H_{16}O_6$. This did not take up water of crystallisation and melted with the immediate elimination of water-vapour. On boiling with hydrochloric acid, it was quantitatively converted into the isomeride previously mentioned. These relationships clearly indicate that geometrical isomerism of the *cis-trans*-type is here being encountered, both the acids $C_{12}H_{16}O_6$ having the structure represented by the formula XXIV, which clearly requires the existence of this kind of isomerism.

The relationships between the various substances obtained by the hydrolysis of ethyl *cyclo*hexane*spiro*di*cyclo*pentanonetricarboxylate and of its sodium derivative are collected together for convenience in table I.

In order to study more closely the contrast presented by the hydrolytic reactions in the dimethyldi*cyclo*pentane and the *cyclo*hexane*spiro*di*cyclo*pentane series, a number of direct comparative experiments were made in order to determine the relative speeds at which the acid-esters of the two types decomposed in the presence of alkali. The substances chosen were the ethyl dihydrogen ester, XXVI,* and the analogous substance in the bridged-

$$\begin{array}{c} CH_3 \\ CH_3 \end{array}\!\!>\!\!C\!\!<\!\!\begin{array}{c} C(CO_2H)\text{--}CH\cdot CO_2H \\ | \\ C(CO_2Et)\cdot CO \end{array}$$
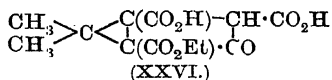
(XXVI.)

spiro-series, namely, the acid-ester XVIII (p. 334). The bridged-ring ester XXVI decomposes under the prolonged action of boiling alcoholic potassium hydroxide, yielding the monobasic acid XIV (p. 333). The bridged-*spiro*-ester XVIII, on the other hand, undergoes fission with the same reagent, giving the *cyclo*hexyl-*cyclo*butane acid XXIV (p. 336).

There is, however, a remarkable difference in the ease with which the two reactions proceed. Thus in one pair of parallel experiments made under comparable conditions, the acid-ester XVIII of the bridged-*spiro*-series gave an 85 per cent. yield of the fission

* This substance was not isolated during the earlier research. Its properties and mode of formation are therefore given in a note at the end of the experimental part of this paper.

TABLE I

C₅H₁₀·C:C(ONa)OEt structure — CO_2Et, $C—CO$, CO_2Et (Yellow, $FeCl_3$ crimson.)

KOH in MeOH cold

CO_2K ; C₅H₁₀·C:C(OK)OEt — CO_2Et, $C—CO$, CO_2Et (Yellow, $FeCl_3$ violet.)

cold HCl → / ← cold KOH

cold HCl → / ← cold NaOH

CO_2Et — $CH·CO_2Et$ — C₅H₁₀·C — $C—CO$ — CO_2Et (M. p. 46—47°, $FeCl_3$ crimson.)

hot HCl short time

CO_2H

CO_2Et — $CH·CO_2Et$ — C₅H₁₀·C — $C—CO$ — CO_2Et (Gum, $FeCl_3$ violet.)

acidified H₂O at 200°

H₂O at 200°

CO_2H — $CH·CO_2H$ — C₅H₁₀·C — $C—CO$ — CO_2Et (M. p. 206° dec., $FeCl_3$ violet.)

KOH in EtOH hot

further action / hot HCl

H₂O at 200°

KOH in EtOH hot

CO_2H / CO_2H

$C_5H_{10}{:}CH{\cdot}C{<}^{CH_2-}_{C(OH)}{>}CO$

(trans, M. p. 206° dec.)

KOH in EtOH hot
further action

$C_5H_{10}{:}CH{\cdot}C{<}^{CH_2-}_{C(OH)}{>}CO$ $\xleftarrow{\;HCl\;}$

$CO_2H\,|\,CO_2H$

(cis, M. p. 145° dec.)

Heat

$C_5H_{10}{:}CH{\cdot}C{<}^{CH_2-}_{C(OH)}{>}CO$

$CO{\cdot}O{\cdot}CO$

(M. p. 155°; anilic acid, m. p. 202° dec.; anil, m. p. 199°.)

Heat | H_2O

AcCl | H_2O

$CO{\cdot}O{\cdot}CO$

$C_5H_{10}{:}C{<}^{C{\cdot}CH}_{C-CO}{>}$
CO_2Et

(M. p. 126°.)

hot HCl
further action

CO_2H

$C_5H_{10}{:}C{<}^{C-CH{\cdot}CO_2H}_{CH-CO}{>}$

(M. p. 234° dec., FeCl₃ crimson.)

CO_2H / CO_2H

$C_5H_{10}{:}C{<}^{C-CH_2}_{C-CO}{>}CO$ and

CO_2Et

$C_5H_{10}{:}C{<}^{C-CH_2}_{C-CO}{>}CO$

(M. p. 104—106°, FeCl₃ no colour.)

H_2O at 200°

AcCl | H_2O

$CO{\cdot}O{\cdot}CO$

$C_5H_{10}{:}C{<}^{C-CH}_{C-CO}{>}$

(M. p. 154°.)

Hot | HCl
long | time

CO_2H

$C_5H_{10}{:}C{<}^{C-CH_2}_{CH{\cdot}CO}{>}$

(M. p. 236°, FeCl₃ no colour.)

product, whilst, on the contrary, the bridged-ring acid-ester XXVI was recovered unchanged to the extent of 93 per cent., only a trace of the monocarboxylic acid being isolated. No fission product of the dimethyldi*cyclo*pentane series was isolated in the course of these experiments.

These experimental comparisons are interesting as showing the extraordinary facility with which the bond (4 : 5) in the bridged-*spiro*-series is broken. They have, however, interest from another point of view. For if they had not been made it would have been possible to advance an explanation of the difference in the ease of fission of the bond (4 : 5) in the two series, based, not on the strain effects of the *cyclo*hexane ring, but on steric hindrance caused by the attached groups. It has already been noticed that it appears to be necessary to have a quaternary carbon atom in the position (4) in order to bring about the fission of the bond (4 : 5) by alkalis. One might assert, therefore, that in the bridged-*spiro*-series the C_5H_{10}: group attached to the carbon atom (5) has the effect of preventing the elimination of the 4-carbethoxyl group. The carbon atoms (4) and (5), therefore, both remain quaternary in the presence of the alkaline reagent, and splitting occurs between them. One would have to assume, of course, that, although the steric effect of the C_5H_{10}: group attached to the carbon atom (5) is sufficiently powerful to prevent the attack of the reagent on the 4-carbethoxyl group, yet, for some reason unknown, it does not inhibit the attack of the same reagent on the bond (4 : 5). In the bridged-ring series, on the contrary, the $(CH_3)_2$: group attached to the carbon atom (5) might not have any appreciable steric effect. Splitting, therefore, might not take place in this case owing to the fact that when the acid-ester XXVI (p. 337) is treated with alcoholic potassium hydroxide, the 4-carbethoxyl group is so quickly eliminated that the carbon atom (4) becomes tertiary before the reagent has had time to react appreciably on the bond (4 : 5).

We were of the opinion at one time that there might be some truth in this way of explaining the phenomena, and it was the desire to test this hypothesis that furnished our chief motive for undertaking the comparative experiments with the acid-esters XXVI and XVIII. It will be seen, however, that the experiments effectively dispose of this explanation, since they show that the 4-carbethoxyl of the acid-ester XXVI is not at all readily eliminated under the experimental conditions employed. We consider this to be strong evidence that the bond (4 : 5) in the bridged-*spiro*-series is actually under considerable strain, much more so than in the bridged-ring series, and that the fission reactions are not to be accounted for as secondary phenomena due to

steric hindrance or other such causes. Several other examples of the splitting of the bond (4:5) in the bridged-*spiro*-series will subsequently be given (sections D and G).

(D) *Hydrolytic Decompositions of the Methylation Products of the Bridged-ring Derivatives IX and XII* (p. 330): *Stability of the* cyclo*Propane Bond* (4:5) *and of the* cyclo*Butane Bond* (2:3).

In the paper on bridged-ring derivatives, to which reference has already been made, interesting results were obtained by methylating the yellow sodium compound IX (p. 330) and subjecting the methyl derivative to alkaline hydrolysis. It was found that the entrance of the methyl group at the carbon atom (2) in XXVII created a point of instability between the carbon atoms (2) and (3), and that fission took place with the formation, apparently, of the *cyclo*propane acid XXVIII, which then underwent a second fission, giving the dibasic lactonic acid XXIX.

$$\begin{array}{c} CH_3 \\ CH_3 \end{array}\!\!>\!\!C\!\!<\!\!\begin{array}{l} C(CO_2Et)\cdot CMe\cdot CO_2Et \\ | \quad\quad\quad | \\ C(CO_2Et)\cdot CO \end{array} \longrightarrow \begin{array}{c} CH_3 \\ CH_3 \end{array}\!\!>\!\!C\!\!<\!\!\begin{array}{l} C(CO_2H)\cdot CHMe\cdot CO_2H \\ | \\ CH\cdot CO_2H \end{array}$$

(XXVII.)   (XXVIII.)

$$\longrightarrow \begin{array}{c} CH_3 \\ CH \end{array}\!\!>\!\!C\!\!<\!\!\begin{array}{l} C(CO_2H)\cdot CHMe\cdot CO_2H \\ CH_2\cdot CO\cdot O \end{array}$$

(XXIX.)
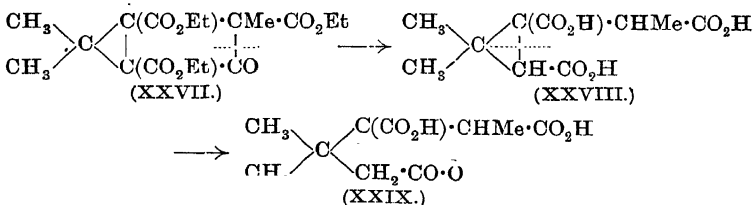
The sodium *spiro*-compound was quite readily methylated by means of methyl iodide. When the ester thus obtained was treated with alcoholic potassium hydroxide, the principal product was a dibasic lactonic acid, evidently a double-fission product, which, however, did not appear to be constituted analogously to the lactonic acid XXIX.

It would appear that there are two quite probable ways in which hydrolytic action might proceed. In the first place, the attack on the ester XXX might commence at the bond adjacent to the

$$C_5H_{10}\!:\!C\!\!<\!\!\begin{array}{l} C(CO_2Et)\cdot CMe\cdot CO_2Et \\ | \quad\quad\quad | \\ C(CO_2Et)\cdot CO \end{array} - \quad C_5H_{10}\!:\!C\!\!<\!\!\begin{array}{l} C(CO_2H)\cdot CHMe\cdot CO_2H \\ | \\ CH\cdot CO_2H \end{array}$$

(XXX.)   (XXXI.)

$$C_5H_{10}\!:\!C\!\!<\!\!\begin{array}{l} C(CO_2H)\cdot CHMe\cdot CO_2H \\ CH_2\cdot CO\cdot O \end{array}$$
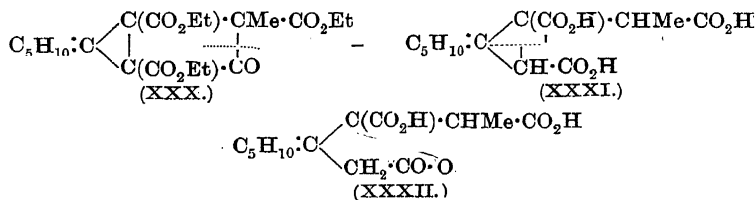
(XXXII.)

methylated residue and give as the first product a *spirocyclo*-propane acid **XXXI**, which is similar to **XXVIII**, and would ultimately yield a lactonic acid **XXXII** strictly analogous to **XXIX**.

On the other hand, we know that the *cyclo*propane bond (4:5) is a very vulnerable point in the molecule of the unmethylated ester **XV** (p. 333), and it can scarcely be supposed that the entrance of a methyl group at the carbon atom (2) would stabilise it to any marked degree. If, in spite of the weakening of the bond (2:3) by the methyl group, the bond (4:5) still remains the most readily attacked part of the molecule, we should expect from the behaviour of the unmethylated ester to obtain a *cyclo*hexyl-*cyclo*butane acid **XXXIII**, which would then split again, this time across the bond beside the methylated residue, giving ultimately a dibasic lactonic acid of the formula **XXXIV**.

$$C_5H_{10}{:}C\underset{\substack{\diagdown\\ C-CO}}{\overset{\substack{\diagup\\ C-CMe{\cdot}CO_2H}}{\Big<}}\quad \overset{CO_2Et}{\underset{CO_2Et}{}}$$

(**XXX.**)

$$\longrightarrow\quad C_5H_{10}{:}CH\diagup\overset{CO_2H}{\underset{C(OH)-CO}{\overset{C-----CMe{\cdot}CO_2H}{\big|}}}$$

$$\underset{CO_2H}{}$$

(**XXXIII.**)

$$\longrightarrow\quad C_5H_{10}{:}CH\diagup\overset{CO_2H}{\underset{CH{\cdot}CO_2H}{\overset{C-CHMe{\cdot}CO{\cdot}O}{\big|}}}$$
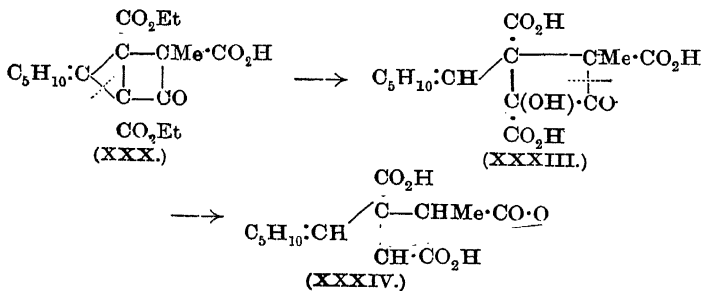
(**XXXIV.**)

In seeking evidence to enable us to decide between the formulæ **XXXII** and **XXXIV**, we made a study of the conditions of anhydride formation of the substance. It will be noticed that both formulæ represent substances which, as they have carboxyl groups attached to contiguous carbon atoms, ought easily to form anhydrides. A substance of the formula **XXXII** would, however, belong to the type of αα′-dimethylsuccinic acid, which yields two stereoisomeric anhydrides corresponding with the two stereoisomeric acids (Bone and Perkin, T., 1896, **69**, 266). The *trans*-acid on treatment with acetyl chloride gives a *trans*-anhydride, which on distillation passes into the anhydride of the *cis*-acid, as shown in Scheme 1.

trans-Acid $\underset{+H_2O}{\overset{-H_2O}{\rightleftarrows}}$ *trans*-anhydride $\overset{Heat}{\longrightarrow}$ *cis*-anhydride $\underset{-H_2O}{\overset{+H_2O}{\rightleftarrows}}$ *cis*-acid.
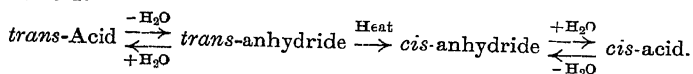
Scheme 1.

The lactonic acid **XXIX** (p. 341), to which **XXXII** is strictly analogous, actually does form two anhydrides related to one

another and to their acids in this way. Consequently, a substance of the formula XXXII should do the same.

On the other hand, in formula XXXIV, the bond uniting the two carboxyl-bearing carbon atoms forms part of a ring, and hence such a substance would be expected to dehydrate in the manner customary with carboxylated alicyclic compounds, the *trans*-acid, in which the carboxyl groups are on opposite sides of the ring, being incapable of forming its own anhydride, but passing on dehydration directly into the anhydride of the *cis*-acid, as indicated in Scheme 2.

$$\textit{trans-}\text{Acid} \xrightarrow{-\text{H}_2\text{O}} \textit{cis-}\text{anhydride} \underset{-\text{H}_2\text{O}}{\overset{+\text{H}_2\text{O}}{\rightleftarrows}} \textit{cis-}\text{acid.}$$
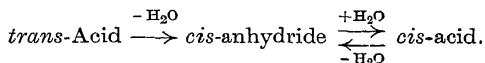
Scheme 2.

Experiment showed that the lactonic acid obtained by the hydrolysis of the ester XXX (p. 342) actually dehydrated in accordance with Scheme 2. The original product of hydrolysis was the *trans*-acid. It did not eliminate water at the melting point, but was readily dehydrated by acetyl chloride. The anhydride formed was the same substance whether the product of dehydration was distilled or not, and on treatment with water yielded the *cis*-acid. This substance melted, with the immediate elimination of water vapour, and was instantly dehydrated by acetyl chloride. These facts point most distinctly to formula XXXIV (p. 342) as representing the true structure of the stereoisomeric acids.

It is obvious, however, that we have by no means exhausted all the possible formulæ in the above considerations, since either of the intermediate compounds XXXI and XXXIII (pp. 341, 342) could split and take up water in a variety of ways. Indeed, besides XXXI and XXXIII, there are a number of other formulæ which the single-fission product might have. When, however, all these possibilities are examined, it would appear that there are only two formulæ besides XXXII and XXXIV (pp. 341, 342) which fulfil the following conditions relating to the *trans*-lactonic acid isolated:

(*a*) That it is a dibasic lactonic acid of the composition $C_{13}H_{18}O_6$, forming in neutral solution a silver salt, $C_{13}H_{16}O_6Ag_2$, and in alkaline solution a barium salt, $(C_{13}H_{17}O_7)_2Ba_3$.

(*b*) That its free carboxyl groups are attached to contiguous carbon atoms. We regard the behaviour of the substance on dehydration as a proof of this.

(*c*) That it is a γ-lactone. Experiment showed that there was an exceedingly strong tendency for the lactone ring to be formed, and in spite of many attempts we were unable to prepare the free hydroxy-acid.

The two formulæ which, along with XXXII and XXXIV, fulfil the above conditions are XXXV and XXXVI.

$$C_5H_{10}{:}C\text{----}C(CO_2H){\cdot}CHMe{\cdot}CO_2H \quad C_5H_{10}{:}C\text{----}C(CO_2H){\cdot}CH_2{\cdot}CO_2H$$
$$O{\cdot}CO{\cdot}CH_2 \qquad\qquad\qquad\qquad O{\cdot}CO{\cdot}CHMe$$
$$(XXXV.) \qquad\qquad\qquad\qquad (XXXVI.)$$
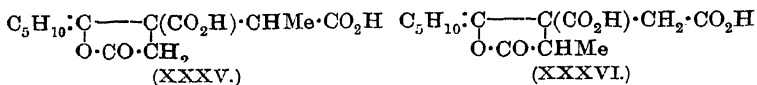
Of these, the first, XXXV, possesses an anhydride-forming group exactly similar to that of the lactonic acid XXXII (p. 341). A substance of the formula XXXV ought, therefore, for reasons given when XXXII was considered, to behave like $\alpha\alpha'$-dimethylsuccinic acid and like the acid XXIX (p. 341), and form anhydrides in accordance with Scheme 1.

The formula XXXVI, on the other hand, does not contain two asymmetric carbon atoms in its anhydride-forming group, and is therefore out of the question.

It will be seen that, of the four possible formulæ, XXXIV (p. 342) is the only one which accords with the facts of the case, namely, that the dehydration of the substance proceeds according to Scheme 2.

It may be added that the *cis*-lactonic acid is converted by boiling hydrochloric acid into the *trans*-isomeride, thus completing the cycle of transformations, which in Scheme 2 is only fragmentary.

The *trans*-lactonic acid XXXIV (p. 342) was not the only product obtained by the alkaline hydrolysis of the methylated ester XXX (p. 342). There was always formed side by side with it a somewhat smaller quantity of a dibasic acid of the composition $C_{13}H_{18}O_6$. Both the dibasic acid and the lactonic acid appeared to be end-products of the reaction; that is to say, they were quite stable towards the reagent used in their preparation. The dibasic acid had properties practically identical with those of the dibasic acid $C_{12}H_{16}O_6$ (XXIV, p. 336), which was obtained by the alkaline hydrolysis of the unmethylated ester XV (p. 333). It has therefore, without much doubt, been formed in a manner precisely analogous to that in which the acid XXIV was produced, and has the structure shown in the formula XXXVII.

$$CO_2H$$
$$C_5H_{10}{:}CH{\cdot}C{<}^{CHMe}_{C(OH)}{>}CO$$
$$CO_2H$$
$$(XXXVII.)$$
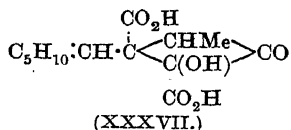
Like the parent substance XXIV, the homologous acid XXXVII was isolated in *cis*- and *trans*-forms, that originally obtained being the *trans*-form.

The formation side by side of the acids XXXIV (p. 342) and XXXVII (p. 344) is readily explained if we accept the view put forward on p. 342, that the *cyclo*propane bond (4:5) of the methylated ester XXX is the first point in the molecule attacked by the alkaline reagent. For, if this is so, the substance XXXIII which is first formed may undergo disruption beside the methylated residue in two ways, corresponding with the two hydrolytic decompositions of ethyl acetoacetate. It may either split the *cyclo*butane ring between the carbon atoms (2) and (3) to give the lactonic acid XXXIV, as shown on p. 342, or it may split between the methyl-bearing carbon atom and the attached carboxyl group, giving the acid XXXVII.

$$C_5H_{10}{:}C{<}{\begin{array}{l}C(CO_2Et){\cdot}CMe{\cdot}CO_2Et\\C(CO_2Et){\cdot}CO\end{array}} \longrightarrow C_5H_{10}{:}CH{<}{\begin{array}{l}C(CO_2H){-}{-}CMe{:}CO_2H\\C(CO_2H)(OH){\cdot}CO\end{array}}$$

$$\text{(XXX.)} \qquad\qquad\qquad \text{(XXXIII.)}$$

$$\longrightarrow \qquad C_5H_{10}{:}CH{<}{\begin{array}{l}C(CO_2H){-}{-}CHMe\\C(CO_2H)(OH){\cdot}CO\end{array}}$$
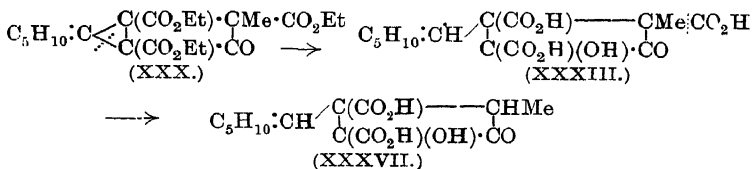
$$\text{(XXXVII.)}$$

It is interesting once again to refer to the parent substance of which the acid XXXVII is the methyl derivative. It was noticed on p. 336 that formulæ XXIV and XXV were equally in harmony with the properties of the substance, but that for reasons there given formula XXIV was to be preferred. We have just seen that the formula which follows from this for the methylated substance enables us to explain the simultaneous production of this compound and of the lactonic acid XXXIV in a very straightforward manner. The alternative formula XXXVIII for the methylated

$$C_5H_{10}{:}CH{\cdot}C{<}{\begin{array}{c}CO_2H\\C(OH)\\{-}CO{-}\end{array}}{>}CHMe$$

$$\qquad\qquad\qquad CO_2H$$

$$\text{(XXXVIII.)}$$
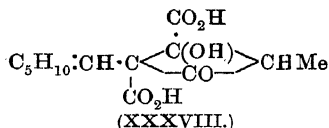
dibasic acid, strictly analogous to the formula XXV, has not this advantage. Such a substance could not be produced side by side with the lactonic acid XXXIV (p. 342), except as a result of the simultaneous occurrence of two totally different sets of reactions; also the lactonic acid which one might expect to be produced along with a compound of the formula XXXVIII would have properties different from those which the lactonic acid isolated was found to possess. We therefore think that we were right in selecting formula XXIV rather than XXV.

The results of the experiments on the alkaline hydrolysis of the

methylation product of the yellow sodium *spiro*-compound are summarised in table II.

These experiments have an interest, inasmuch as they confirm, and even emphasise, the remarkable instability of the bond (4 : 5) in the bridged-*spiro*-series.   For, in spite of the fact that the entrance of the methyl group at the carbon atom (2) of the methylated ester XXX creates a point of instability between the carbon atoms (2) and (3), the reagent commences its attack, not at the bond (2 : 3), but at the bond (4 : 5).

(E) *Reduction of the Monocarboxylated Bridged-ring Derivatives XIV and XXIII* (pp. 333 and 335). *Stability of the Bridge-bond* (1 : 4).

When the bridged-ring acid XIV is reduced by sodium amalgam, there is formed a *cyclo*pentane acid XXXIX which contains two more atoms of hydrogen than the original acid.   The reduction product is a ketonic acid, and on further reduction yields the corresponding hydroxy-acid XL.   The fact that the ketonic acid has been formed by the addition of hydrogen at the bridge-bond (1 : 4) is shown (*loc. cit.*) by the production on oxidising with nitric acid of $\beta\beta$-dimethylglutaric acid and *as*-dimethylsuccinic acid.   The reduction is therefore to be represented thus :

$$\underset{(XIV.)}{\underset{CH_3}{CH_3}>C<\overset{\overset{CO_2H}{|}}{\underset{CH\cdot CO}{C{-}CH}}} \rightarrow \underset{(XXXIX.)}{\underset{CH_3}{CH_3}>C<\overset{CO_2H}{\underset{CH_2\cdot CO}{CH{-}CH_2}}} \rightarrow \underset{(XL.)}{\underset{CH_3}{CH_3}>C<\overset{CO_2H}{\underset{CH_2\cdot CH\cdot OH}{CH{-}CH_2}}}$$
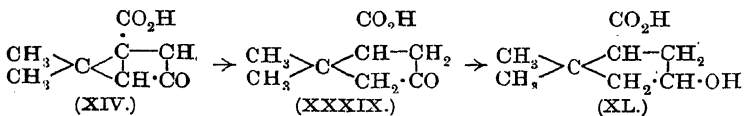
The remarkable feature of this reaction is that the bond (1 : 4) is actually more susceptible of attack by the reducing agent than is the carbonyl group, and that, consequently, the bridged hydroxy-acid XLI cannot be isolated.

$$\underset{(XLI.)}{\underset{CH_3}{CH_3}>C<\overset{C(CO_2H)\cdot CH_2}{\underset{CH{-}{-}{-}CH\cdot OH}{|}}} \qquad \underset{(XLII.)}{C_5H_{10}:C<\overset{C(CO_2H)\cdot CH_2}{\underset{CH{-}{-}{-}CH\cdot OH}{|}}}$$
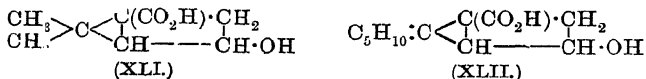
A series of experiments, using the monobasic acid XXIII, yielded precisely comparable results.   In spite of careful search among the products of reductions carried out under varying conditions, no bridged hydroxy-acid of the formula XLII was isolated.

The first product of the action of sodium amalgam on the ketonic acid XXIII (p. 335) was a substance which contained two atoms of added hydrogen.   It did not appear to react with acetyl chloride, but readily gave a semicarbazone.   On subjecting it to further

TABLE II.

$$C_5H_{10}{:}C\diagdown\genfrac{}{}{0pt}{}{\overset{CO_2Et}{C}{-}CMe{\cdot}CO_2Et}{\underset{CO_2Et}{C}{-}CO}$$

(liquid, dec. on distillation.)

KOH in alcohol ↓

Branching scheme:

$$C_5H_{10}{:}CH{\cdot}CH{\cdot}C\diagdown\genfrac{}{}{0pt}{}{CHMe}{C(OH)}{>}CO$$
with $\overset{CO_2H}{\underset{\dot C O_2H}{|}}$

(trans, M. p. 185° dec.)

Heat

OH–   CO₂H·CH   OH–   –CHMe·CO₂H   C₅H₁₀   –CHMe·CO₂H
H   ĊH   H   CH   ĊO₂H
      CO₂H·ĊH   CO₂H   ȮO₂H   CO₂H   OH–

(trans, as salts only)   (cis, as salts only.)

HCl on salts ↓↑ NaOH   HCl on salts ↓↑ NaOH

$$H_{10}{\cdot}CH{\cdot}CH{\cdot}C\diagdown\genfrac{}{}{0pt}{}{CHMe{\cdot}CO}{CH{-}\!\!-\!\!O}$$
CO₂H

(trans, M. p. 172°.)

AcCl ↓

$$C_5H_{10}{\cdot}CH{\cdot}C{\cdot}C\diagdown\genfrac{}{}{0pt}{}{CHMe{\cdot}CO}{CH{-}\!\!-\!\!O}$$
CO·O·CO

(M. p. 170°.)

hot HCl ←

$$C_5H_{10}{\cdot}CH{\cdot}CH{\cdot}C\diagdown\genfrac{}{}{0pt}{}{CHMe{\cdot}CO}{CH{-}\!\!-\!\!O}$$
CO₂H

(cis, M. p. 152°.)

H₂O ↑↓ AcCl

Left branch:

Hot HCl →

$$C_5H_{10}{\cdot}CH{\cdot}C{\cdot}C\diagdown\genfrac{}{}{0pt}{}{CHMe}{C(OH)}{>}CO$$
with $\overset{CO_2H}{\underset{CO_2H}{|}}$

(cis, M. p. 148° dec.)

Heat ↑↓ H₂O

$$C_5H_{10}{\cdot}CH{\cdot}C{\cdot}C\diagdown\genfrac{}{}{0pt}{}{CHMe}{C(OH)}{>}CO$$
CO·O·CO

(M. p. 158°.)

reduction by sodium amalgam, two more atoms of hydrogen were taken up, and there was formed a substance which gave an acetyl derivative on treatment with acetyl chloride. The successive reductions are therefore apparently analogous in the dimethyldi*cyclo*pentane and *cyclo*hexanes*piro*di*cyclo*pentane series, and in the latter case may be represented thus:

$$C_5H_{10}{:}C{<}\begin{matrix}\overset{CO_2H}{\overset{\bullet}{C}{-}CH_2}\\CH{\cdot}CO\end{matrix} \rightarrow C_5H_{10}{:}C{<}\begin{matrix}\overset{CO_2H}{\overset{\bullet}{C}H{-}CH_2}\\CH_2{\cdot}CO\end{matrix} \rightarrow C_5H_{10}{:}C{<}\begin{matrix}\overset{CO_2H}{\overset{\bullet}{C}H{-}CH_2}\\CH_2{\cdot}CH{\cdot}OH\end{matrix}$$

(XXIII).   (XLIII.)   (XLIV.)
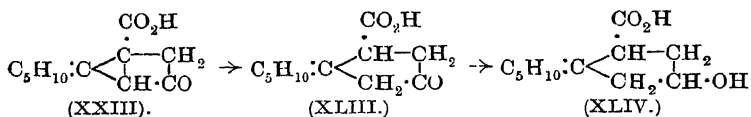
The fact that it was really the bond (1:4), and not the bond (4:5) or the bond (5:1), which had been broken by the reducing agent was clearly proved by the manner in which the reduced substances behaved with oxidising agents. These experiments are dealt with in Section F.

In our earliest experiments on the reduction of the bridged ketonic acid XXIII, we used conditions which were known to give a good yield of the reduced acid XXXIX when applied to the reduction of the bridged ketonic acid XIV. As a result, we obtained a product of indefinite melting point, which proved to be a mixture of the ketonic and hydroxy-acids XLIII and XLIV. It was therefore apparent that the reduction was proceeding more easily in the bridged-*spiro*-series than in the bridged-ring series.

In order to establish this point more definitely, a series of comparative experiments were instituted. In the first place, the bridged ketonic acid XIV (p. 333) was reduced under standard conditions for different lengths of time, and the products were isolated. They were, in general, a mixture of three acids, XIV, XXXIX, and XL. The proportion of hydroxyl group in this mixture was determined by estimating the acetic acid obtained by acetylation and subsequent hydrolysis. This method was found to give good results when applied to the pure hydroxy-acid XLIV. In this way, a certain time of reduction was discovered during which no appreciable quantity of hydroxy-acid was produced. The hydrogen content was determined by combustion, and it was found that the formation of hydroxy-acid began to be appreciable after the addition of about 1·7 atoms of hydrogen to the molecule. A similar set of experiments with the bridged ketonic acid of the *spiro*-series showed that the production of hydroxy-acid in this case became appreciable only after the addition of about 1·9 atoms of hydrogen to the molecule. The two bridged ketonic acids XIV and XXIII were then reduced under the same standard conditions for a certain length of time, the same in both cases, sufficiently short to ensure

that in neither case would any measurable amount of hydroxy-acid be formed. The products were then isolated and the hydrogen contents determined by combustion. Several pairs of experiments were made with different lengths of time, and the results obtained

Fig. (viii).

Fission of the bridge-bond 1 : 4.
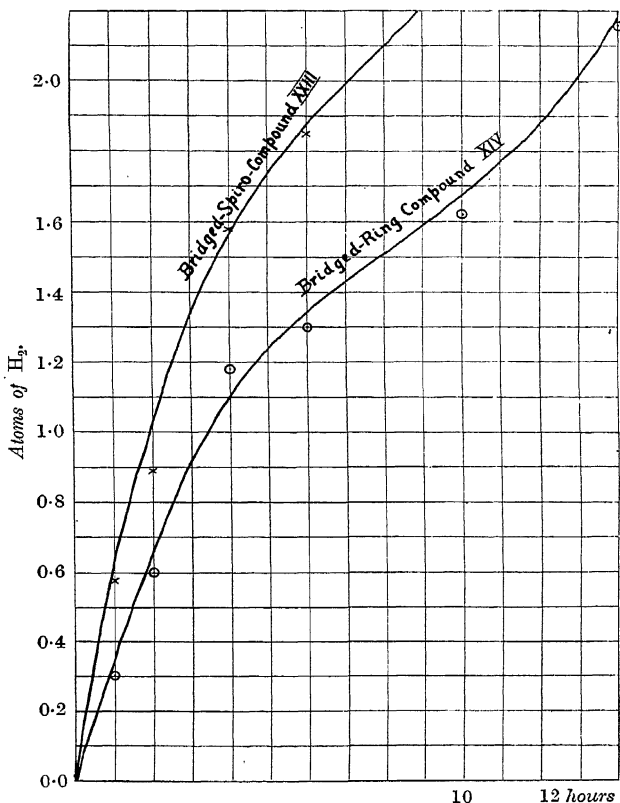
are given in the experimental part of this paper (p. 375). The figures lie fairly well on smooth but widely separated curves (Fig. viii), and, graphically interpolated, they show that if we take the time required for a 50 per cent. conversion, that is, the time during which the molecule of the bridged acid takes up one

atom of hydrogen, as the standard of comparison, then this time, in the case of the *spiro*-acid XXIII, is about 0·55 times as long as in the case of the ring derivative XIV.   That is to say, the periods of half-change are in the ratio of approximately 1·8:1.

As a check on this result, the reduced acids XXXIX and XLIII (pp. 346 and 348) were prepared in a state of purity and further reduced under standard conditions for different lengths of time. The figures obtained in these experiments (p. 375) lie, with slight irregularities, on one and the same curve (Fig. ix).   The periods

FIG. (ix).

Reduction of the ketone group.
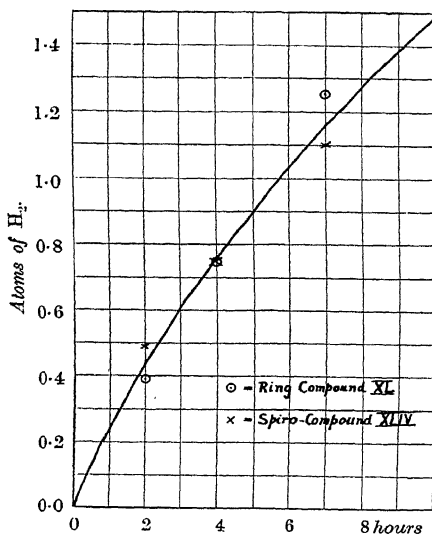
of half-change are therefore as 1:1 as nearly as the experimental figures can be interpreted.

Thus there appears to be a very real difference in the ease of reduction of the monocarboxylic acids of the bridged-ring- and bridged-*spiro*-series.   It will be noticed that the difference is in the sense anticipated from theoretical considerations (see Section A).   It also would appear to be of the correct order of magnitude.   For whilst the first-order effect, that on the bond (5:1), is manifested by a reaction which proceeds at a considerable speed in one series, but does not go at all in the other so far as

can be detected, both the second-order effects, that is, those on the bonds (1:2) and (1:4), exhibit themselves experimentally as moderate differences in reaction-velocities which are finite quantities in both the series. The third-order effect, that on the bond (2:3), was not detected experimentally.

(F) *Oxidation of the Fission-Products Derived from the Bridged-spiro-compound XII* (p. 330).

All the products of fission of the *cyclo*hexane*spirodicyclo*pentane ring structure so far considered belong to one or other of the three following classes:

(1) Substances in which the bridge-bond (1:4) only has been broken.

(2) Those in which the *cyclo*propane-bond (4:5) only has been broken.

(3) Those in which the *cyclo*propane-bond (4:5) and the *cyclo*butane-bond (2:3) have both been broken.

In order, if possible, to obtain some confirmatory evidence regarding the constitutions of these substances, at least one typical example from each class was subjected to the action of oxidising agents.

In class (1) the first substance taken was the *cyclo*hexane*spiro-cyclo*pentanone acid XLIII (p. 348). By far the most suitable reagent in this case is nitric acid. Dilute nitric acid, however, appears to have little action on the substance. With hot concentrated nitric acid a dibasic acid of the composition $C_8H_{12}O_4$ was obtained. This substance when distilled gave off carbon dioxide with the formation of *cyclo*hexanecarboxylic acid (hexahydrobenzoic acid). The dibasic acid is therefore evidently *cyclo*hexane-1:1-dicarboxylic acid XLV. The same dicarboxylic acid was obtained

$$C_5H_{10}{:}C{<}^{CH(CO_2H)\cdot CH_2}_{CH_2\text{------}CO} \quad \xrightarrow{HNO_3} \quad C_5H_{10}{:}C{<}^{CO_2H}_{CO_2H}$$

(XLIII.)   (XLV.)
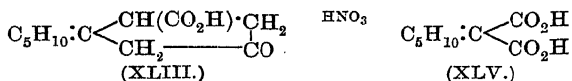
when the hydroxy-acid XLIV (p. 348) was used in place of the ketonic acid.

These experiments are interesting as leaving little room for doubt that the bond broken in the reduction of the bridged-ketonic acid XXIII (p. 335) was actually the bond (1:4).

The example taken from class (2) was the *trans-cyclo*hexylcyclobutane acid XXIV (p. 336). In this case nitric acid appeared to be without effect. Warm alkaline permanganate was, however, quickly decolorised. The acid product was a liquid substance which

distilled apparently without a serious amount of decomposition and was identified as *cyclo*hexanecarboxylic acid XLVI:

$$C_5H_{10}{:}CH{\cdot}C\underset{\underset{\underset{CO_2H}{|}}{C(OH)}}{\overset{\overset{\overset{CO_2H}{|}}{{<}-CH_2-}}{{<}}}{>}CO \quad \overset{KMnO_4}{\longrightarrow} \quad C_5H_{10}{:}CH{\cdot}CO_2H$$

$$(XXIV.) \hspace{5cm} (XLVI.)$$
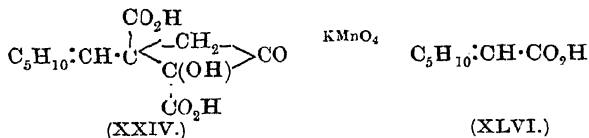
The member of the series (3) experimented on was the *trans-β-cyclo*hexyl-*n*-butane lactonic acid XXXIV (p. 342). This acid was also unacted on by nitric acid, and required an alkaline solution of permanganate kept at above 70° to oxidise it at all rapidly. The product was, as in the former case, *cyclo*hexylcarboxylic acid:

$$C_5H_{10}{:}CH{\cdot}\underset{\underset{CH(OH){\cdot}CO_2H}{|}}{\overset{\overset{Me{\cdot}CH{\cdot}CO_2H}{|}}{C}}{\cdot}CO_2H \quad \overset{KMnO_4}{\longrightarrow} \quad C_5H_{10}{:}CH{\cdot}CO_2H$$

$$(\text{Hydroxy-acid of XXXIV.}) \hspace{3cm} (XLVI.)$$
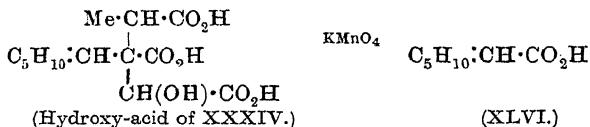
Both these oxidations with permanganate were carried out under various conditions, and in both cases the products were carefully examined for any traces of polybasic or lactonic acids, in which two side-chains might be attached to the *cyclo*hexane carbon atom. No such products were detected, and, in view of the formulæ of the oxidised substances, none would be expected. On the other hand, if, for example, in the production of the *cyclo*hexyl*cyclo*butane acid XXIV (p. 336) some bond in the di*cyclo*pentane structure other than one of those attached to the spirane carbon atom had been ruptured, one would expect to find products with two side-chains among the oxidation products.

The *cyclo*hexanecarboxylic acid XLVI obtained in the course of the above experiments appeared on careful examination to be in all cases identical with the product obtained by the reduction of benzoic acid.

The various reactions by which the di*cyclo*pentane ring in the original bridged-*spiro*-compound XII (p. 330) has been broken down forming ultimately *cyclo*hexanecarboxylic acid are summarised for convenience in table III.

TABLE III.

$$C_5H_{10}{:}C{<}\begin{matrix}CO_2Et\\C{\cdot}C(ONa){\cdot}OEt\\C{-}CO\end{matrix}$$
CO_2Et
(Yellow solid.)

CO_2H

$$C_5H_{10}{:}C{<}\begin{matrix}CO_2H\\C{-}Y{\cdots}_2\\CH{\cdot}CO\end{matrix}$$

(M. p. 236°; semicarbazone, m. p. 259° dec.)

sodium amalgam

$$C_5H_{10}{:}C{<}\begin{matrix}CO_2H\\CH{-}CH_2\\CH_2{-}CO\end{matrix}$$

(M. p. 136—138°; semicarbazone, m. p. 210° dec.)

sodium amalgam

$$C_5H_{10}{:}C{<}\begin{matrix}CO_2H\\CH{-}CH_2\\CH_2{-}CH{\cdot}OH\end{matrix}$$

(M. p. 125—127°; acetyl derivative, m. p. 158—163°.)

$\xrightarrow{HNO_3}$

KOH in alcohol

$$C_5H_{10}{:}CH{-}\begin{matrix}CO_2H\\C{-}CH_2\\C(OH){\cdot}CO\end{matrix}$$
CO_2H
(M. p. 206° dec.)

$$C_5H_{10}{:}C{<}\begin{matrix}CO_2H\\CO_2H\end{matrix}$$
(M. p. 207° dec.)

$\xrightarrow{MeI}$

$$C_5H_{10}{:}C{<}\begin{matrix}CO_2Et\\Me{\cdot}CO_2Et\end{matrix}$$
CO_2Et
(Colourless oil.)

KOH in alcohol

$$C_5H_{10}{:}CH{-}\begin{matrix}CO_2H\\C{\cdot}CHMe{\cdot}CO\\CH{-}O\end{matrix}$$
CO_2H
(M. p. 172°.)

$KMnO_4$

$\xrightarrow{heat}$

$C_5H_{10}{:}CH{\cdot}CH{\cdot}CO_2H$
(cycloHexanecarboxylic acid.)

(G) *Examination of the By-products obtained in the Preparation of the Bridged-spiro-compound XII* (p. 330): *Isolation of Products of Fission Derived from this Substance through Side Reactions.*

During the preparation of the yellow sodium compound XII (p. 330) there was formed a considerable quantity of an oily by-product from which a number of acids were obtained by hydrolysis with hydrochloric acid. Amongst those isolated were *n*-butyric acid, *cyclo*hexane-1 : 1-diacetic acid, and *trans-cyclo*hexane*spirocyclo*propane-1 : 2-dicarboxylic acid. The formation of these acids is evidently traceable to the presence in the crude ethyl dibromo-*cyclo*hexanediacetate used for the condensation of the corresponding monobromo-ester, of the unbrominated ester, and of ethyl bromide as impurities. There was also obtained a *cyclo*hexane*spirocyclo*propane acid of the formula XLVII. This substance proved to be identical with the acid obtained by the action of acid hydrolysing

$$C_5H_{10}{:}C{<}{\stackrel{\textstyle C(CO_2H)\cdot CH_2\cdot CO_2H}{CH\cdot CO_2H}}$$
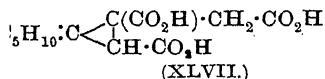
(XLVII.)

agents on the tetra-ethyl *spirocyclo*propane ester XI (p. 330), which clearly establishes the constitution of the compound.

In addition to the above-mentioned acids there were isolated two others to which the formulæ XLVIII and XLIX have been

$$C_5H_{10}{:}C{<}{\stackrel{\textstyle \overset{CO_2H}{\overset{\textstyle |}{C}}\text{---}CHEt}{\underset{\textstyle }{CH\cdot CO}}}$$

(XLVIII.)

$$C_5H_{10}{:}CH\cdot\overset{\textstyle Et\cdot CH-\text{ ----}CO}{\underset{\textstyle CH(CO_2H)\cdot O}{C\cdot CO_2H}}$$

(XLIX.)
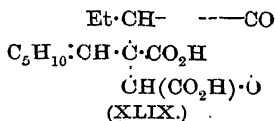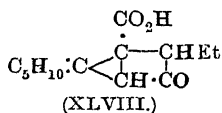
assigned. These are clearly the products respectively of acid and of alkaline hydrolysis of the ethylated ester L. This ester is doubt-

$$C_5H_{10}{:}C{<}{\stackrel{\textstyle C(CO_2Et)\cdot CEt\cdot CO_2Et}{C(CO_2Et)\cdot CO}}$$

(L.)
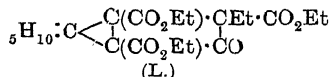
less produced by the action of ethyl bromide on the yellow sodium compound XII, and apparently behaves towards alkaline hydrolysing agents similarly to the corresponding methylation product XXX (p. 342). We did not investigate the action of acids on the methyl derivative XXX, but the corresponding substance XXVII (p. 341) of the dimethyldi*cyclo*pentane series was found (*loc. cit.*) to yield with acid hydrolysing agents a monocarboxylic acid, to which XLVIII is strictly analogous.

The most interesting of these substances is the fission product XLIX of the ester L, and it is of interest to examine what possibilities there are of alkaline hydrolysis of the ester L taking place. No hydrolysis to a lactone of hydroxy-ester would be likely to occur in the anhydrous alcoholic solution in which the oily by-product was formed. The oil was, however, separated from the sodium compound XII by means of 95 per cent. alcohol, and, since some sodium ethoxide would certainly be adhering to the crude sodium compound, the alcoholic washings would contain sodium hydroxide, which must have brought about the fission of the ethylated ester L.

The lactonic acid XLIX was found to possess properties practically identical with those of its prototype, the fission product XXXIV (p. 342), of the methylated bridged ester XXX. Like the lactonic acid XXXIV, it was isolated in *cis*- and *trans*-forms, the substance originally obtained being the *trans*-form. One notable point of difference was noticed between these compounds and the methylated lactonic acids previously obtained. The ethylated *cis*-lactonic acid differed from the *trans*-form, and from both forms of the lactonic acid XXXIV, in the fact that it was found possible to isolate from it the free tribasic hydroxy-acid. This substance was, however, very unstable. It slowly gave up water when exposed to air at the ordinary temperature, the product being the *cis*-lactonic acid. On boiling with hydrochloric acid it was converted into the *trans*-lactonic acid. The other relationships between these ethylated products may be seen by reference to table IV, in which they are shown in relation to the ethylated ester L, the decompositions of which form another example of the great ease with which the bond (4:5) is ruptured by alkalis.

Experimental.

(a) *Condensation of Ethyl Dibromocyclohexane*-1:1-*diacetate with Ethyl Sodiomalonate.*

*cyclo*Hexane-1:1-diacetic acid was prepared for use in these experiments by the method given by Thole and Thorpe (T., 1911, **99**, 422).

Ethyl Dibromocyclohexane-1:1-*diacetate.*—The bromination of the acid was effected by the Hell-Volhard-Zelinsky method as described in Part I. of this series. The neutral product contained about 80 per cent. of dibromo-ester.

TABLE IV.

C_5H_{10}

$\overset{OH}{\underset{CO_2H}{\mid}}$ — $\overset{H}{\underset{CO_2H}{\mid}}$ — CHEt·CO_2H

(*cis*, slowly decomposes.)

NaOH ⇌ spontaneously

C_5H_{10}:CH·C$\overset{CHEt·CO}{\underset{CO_2H \mid CO_2H}{<}}$CH—O

(*cis*, M. p. 198° dec.)

AcCl

H_2O

C_5H_{10}:CH·C$\overset{CHEt·CO}{\underset{CO·O·CO}{<}}$CH—O

(M. p. 154°.)

hot HCl

hot HCl

NaOH

C_5H_{10}CH

$\overset{OH}{\underset{CO_2H}{\mid}}$ — $\overset{H}{\underset{CO_2H}{\mid}}$ — CHEt·CO_2H

(*trans*, as salts only.)

HCl on salts ⇌ NaOH

C_5H_{10}·CH·C$\overset{CHEt·CO}{\underset{CO_2H \mid CO_2H}{<}}$CH—O

(*trans*, M. p. 149°.)

AcCl

NaOH →

C_5H_{10}:C$\overset{CO_2Et}{<}$C$\overset{CEt·CO_2Et}{\underset{CO_2Et}{\mid}}$CO

(By ethyl bromide on XII.)

HCl →

C_5H_{10}:C$\overset{CO_2H}{<}$C$\overset{CHEt}{\underset{CH·CO}{\mid}}$

(M. p. 191—194°.)

Ethyl cyclo*Hexane*spiro-1-*methyl*cyclo*propane*-1 : 1' : 1' : 2-*tetra-carboxylate* (XI, p. 330).

Forty-six grams of the crude dibromo-ester were added to a solution, in 60 grams of alcohol, of 4·6 grams of sodium and 32 grams of ethyl malonate. The solution was boiled for three hours, and then poured into dilute hydrochloric acid. The oil was extracted with ether and the extract washed with a solution of sodium carbonate, dried, and distilled.

The ester was obtained as a colourless liquid which on redistillation boiled at 250—260°/10 mm. On boiling with hydrochloric acid it was hydrolysed with the formation of the tricarboxylic acid (XLVII, p. 354), dealt with on p. 379 :

0·1209 gave 0·2708 CO_2 and 0·0849 H_2O. C = 61·09 ; H = 7·80.
$C_{21}H_{32}O_8$ requires C = 61·2 ; H = 7·8 per cent.

(b) *Formation of the Bridged*-spiro-*ester and its Sodium Compound.*

The formation of the bridged-*spiro*-compound by the condensation of the above-mentioned tetraethyl ester with itself has already been referred to in the Introduction (Section B). The compound was, however, usually prepared direct from the dibromo-ester by treating it with ethyl malonate and excess of sodium ethoxide. Many experiments were made in order to determine the best conditions.

*Ethyl Sodio*cyclo*hexane*spiro*dicyclopentan*-3-one-1 : 2 : 4-*tricarboxylate* (XII, p. 330).

Nine grams of sodium dissolved in 140 grams of absolute alcohol were treated with 30 grams of ethyl malonate. The solution was carefully under-cooled to about 35°, and 40 grams of dibromo-ester were gradually added, the temperature being kept below 40°. Half an hour after the addition was complete the liquid was heated on a steam-bath and kept boiling for thirty hours. At the end of that time the greater part of the alcohol was boiled off, and water added to the residue in the flask. The mixture was then shaken vigorously and filtered by the aid of the pump. In these circumstances the whole of the oil precipitated by the water adhered to the solid sodium compound. The filtrate, which gave no precipitate on acidification, was discarded. The purification of the sodium compound was effected by washing on the filter with 95 per cent. alcohol, and

finally by triturating with the same solvent until the weight of the dry solid was not altered on repeating the treatment. The alcoholic filtrates contained the oily by-product. (Section j, p. 377.)

The sodium compound was obtained as a bright yellow insoluble substance which gave a crimson colour with aqueous ferric chloride containing a trace of alcohol:

0·3132 gave 0·0590 Na_2SO_4. $Na = 6·10$.

$C_{19}H_{25}O_7Na$ requires $Na = 5·93$ per cent.

Ethyl cyclo*Hexane*spiro*dicyclopentan-3-one-1 : 2 : 4-tricarb-oxylate* (XV, p. 333).

When the yellow sodium compound was shaken with cold dilute aqueous hydrochloric acid and ether it passed quickly into solution, the yellow colour being discharged. The ethereal layer, on drying and evaporating the solvent, yielded a mass of crystals melting at 46—47°.

The ester was exceedingly readily soluble in the usual organic solvents, and did not appear capable of being easily recrystallised. It gave a crimson colour with ferric chloride, and on treating with cold aqueous sodium hydroxide yielded the original sodium compound:

0·1331 gave 0·3036 CO_2 and 0·0842 H_2O. $C = 62·21$; $H = 7·03$.

$C_{19}H_{26}O_7$ requires $C = 62·3$; $H = 7·1$ per cent.

(c) *Comparative Experiments on the Formation of the Bridged-ring- and Bridged-*spiro*-compounds* (IX and XII, p. 330).

$\beta\beta$-Dimethylglutaric acid was prepared by the method of Thole and Thorpe (T., 1911, **99**, 422).

Ethyl Dibromodimethylglutarate.—The acid was first converted into its anhydride (T., 1899, **75**, 48), which was then brominated (T., 1901, **79**, 776). The dibromo-ester was redistilled and collected for use in subsequent experiments at 182—185°/24 mm.

Ethyl 1 : 3 : 3-*Trimethyl*cyclo*propane-1 : 1′ : 1′ : 2-tetracarboxylate.*

This ester was prepared by condensing the dibromo-ester with ethyl sodiomalonate in alcoholic solution under the conditions used by Perkin and Thorpe (*ibid.*) and purified by distillation, the fraction boiling at 231—236°/34 mm. being taken as sufficiently pure for the experiments hereunder described.

Ethyl trimethyl*cyclo*propanetetracarboxylate and ethyl *cyclo-*

hexane*spiro*methyl*cyclo*propanetetracarboxylate were then employed
in a series of experiments, which were carried out with the object
of determining the relative speeds with which the two esters under-
went internal condensation in the presence of sodium ethoxide. The
method was as follows: One molecular proportion of each ester was
treated with two atomic proportions of sodium dissolved in fifteen
molecular proportions of absolute ethyl alcohol. The solutions
were kept in a thermostat for known lengths of time, after which
the alcohol was boiled off under diminished pressure, and water
was added. The precipitates were then collected, washed with
alcohol, dried, and weighed.

The following percentage yields of the sodium compounds IX
and XII (p. 330) were obtained, the temperature being 75°:

TABLE V.

Time (hours).	Bridged-ring-compound, IX. (Per cent.)	Bridged-*spiro*-compound, XII (Per cent.)
1·0	49·8	10·1
2·0	64·7	17·9
4·0	73·0	25·5
7·0	76·6	32·4
10·0	75·3	32·9
14·0	75·3	—
24·0		37·7

(d) *Hydrolysis of the Bridged-*spiro*-ester and of its Yellow
Sodium Compound.*

The remarkable diversity in the characters of the substances
which can be obtained by hydrolysing the yellow sodium *spiro*-
compound or the corresponding free ester under different conditions
has already been alluded to in the Introduction. The following
is a summary of the principal experimental details.

*Diethyl Potassium Potassio*cyclohexane*spiro*dicyclo*pentan-3-
one-1 : 2 : 4-tricarboxylate* (XVI, p. 333).

When the original yellow sodium compound was left in contact
with cold alcoholic potassium hydroxide for ten hours, it gradually
dissolved, and a canary-yellow potassium salt separated.

This compound was found to be insoluble in water, but quite
appreciably soluble in methyl alcohol. When recrystallised from
a large bulk of this solvent, it separated in long, yellow needles,
which gave a violet colour with ferric chloride:

0·1354 gave 0·0580 K_2SO_4. $K = 19·16$.

$C_{17}H_{20}O_7K_2$ requires $K = 18·8$ per cent.

Diethyl Hydrogen cyclo*Hexane*spiro*dicyclopentan*-3-*one*-
1 : 2 : 4-*tricarboxylate* (XVII, p. 333).

When the potassium salt was treated with cold dilute hydro-
chloric acid, a gummy precipitate was obtained. This could not
be induced to crystallise, and on distillation underwent extensive
decomposition. It was therefore extracted with pure ether, and,
after drying and evaporating the solvent, left for some days in an
exhausted desiccator:

0·1249 gave 0·2751 CO_2 and 0·0730 H_2O. C = 60·07; H = 6·50.
$C_{17}H_{22}O_7$ requires C = 60·4; H = 6·5 per cent.

This acid-ester is also the first product of the action of boiling
hydrochloric acid on the triethyl ester (XV, p. 333), as is proved
by the following experiment. The yellow sodium compound was
boiled with 20 per cent. hydrochloric acid for one hour. The
liquid was evaporated, and the residue dissolved in the minimal
quantity of water. The hot aqueous solution was rapidly cooled,
and the oily precipitate which separated was collected by pouring
the liquid through a wet filter. The oil on the filter was then
washed through with alcohol, and caused to crystallise as com-
pletely as possible from 15 per cent. alcohol. The crystals con-
sisted of the ethyl hydrogen ester XXI (p. 335). The ultimate
oily residue from these crystallisations was dissolved in methyl
alcohol and treated with a slight excess of cold methyl-alcoholic
potassium hydroxide. The yellow precipitate which immediately
separated was collected and recrystallised from methyl alcohol.
On analysis, it gave K = 19·03, whilst the free acid-ester obtained
on acidification gave C = 60·21, H = 6·60 per cent.

With ferric chloride, the acid-ester gave a violet coloration.
Cold methyl-alcoholic potassium hydroxide converted it into the
potassium compound. It distilled at about 200—260°/23 mm.,
with, however, considerable decomposition. Attempts were made
to hydrolyse the gummy distillate both by acids and by alkalis,
but no pure substance was isolated from the products.

Ethyl Dihydrogen cyclo*Hexane*spiro*dicyclopentan*-3-*one*-
1 : 2 : 4-*tricarboxylate* (XVIII, p. 334).

Five grams of the yellow sodium compound were suspended in
20 c.c. of 3N-ethyl-alcoholic potassium hydroxide, and the mixture
was boiled until the yellow colour was discharged. The colourless
precipitate, which was very hygroscopic, was collected as rapidly
as possible and drained on porous porcelain in a desiccator. It

was then dissolved in a small quantity of water and decomposed with hydrochloric acid. The acid which separated out was re-crystallised from water. The potassium salt XVI may be used in place of the sodium compound in this preparation.

The same acid-ester may also be obtained by acid hydrolysis of the triethyl ester (XV, p. 333) or of its sodium compound. Thus, when the sodium compound was boiled for one hour with 20 per cent. hydrochloric acid, and the acid-esters XVII and XXI separated by precipitating them together as an oil in the manner described on p. 360, it was found that in the filtrate from the oil there were present two crystalline substances. These were isolated by treating the solution, after concentration, with sufficient concentrated hydrochloric acid to clear the turbidity. The crystals which were then deposited from solution were separated by fractionally crystallising from water into the acid-ester XVIII and the dibasic acid XXII, the latter being the more readily soluble.

The acid-ester formed long, colourless needles, which melted and decomposed at 206°. It gave a bluish-violet colour with ferric chloride:

0·1298 gave 0·2745 CO_2 and 0·0683 H_2O.   C=57·68; H=5·84.

$C_{15}H_{18}O_7$ requires C=58·1; H=5·8 per cent.

The *anhydro-ester,*

$$C_5H_{10}{:}C{<}\begin{array}{c} CO{-\!\!-}O{-\!\!-}CO \\ \overset{\centerdot}{C}{-\!\!\!-\!\!\!-\!\!\!-}\overset{|}{C}H \\ \underset{C(CO_2Et)\centerdot\overset{|}{C}O}{|} \end{array}$$
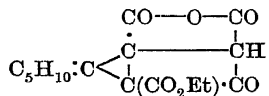
was prepared by treating the acid-ester at 100° for one hour with acetyl chloride in a closed flask. The residue obtained on evaporation was crystallised from ether. The crystalline anhydride melted at 126°, and was converted into the original acid-ester on boiling with water:

0·0751 gave 0·1705 CO_2 and 0·0385 H_2O.   C=61·92; H=5·70.

$C_{15}H_{16}O_6$ requires C=61·6; H=5·5 per cent.

Ethyl Hydrogen 5-cyclo*H*exane*spiro*dicyclopentan-3-one-1 : 4-*dicarboxylate* (XXI, p. 335).

The formation of this substance has already been alluded to on p. 360. It is best prepared by boiling the triethyl ester (XV, p. 333) with 20 per cent. hydrochloric acid for five hours, or by boiling the acid-ester (XVIII, p. 334) with the same reagent for two hours. In either case, the product obtained on evaporation was found to be a mixture of three acids. It was crystallised from

the minimal quantity of boiling 50 per cent. ethyl alcohol. The crystals which separated consisted principally of the monobasic acid (XXIII, p. 335), and were collected, the filtrate being then evaporated until most of the alcohol had been removed. It was then cooled as rapidly as possible, and the oil which separated was collected on a wet filter. The filtrate, on concentrating and mixing with concentrated hydrochloric acid, deposited the dibasic acid (XXII, p. 335). The oil on the filter was dissolved in alcohol and recrystallised several times from a mixture of alcohol and water.

The acid-ester obtained in this way melted at 104—106°, and gave no colour with ferric chloride. It did not decompose appreciably when heated to 250°:

0·0887 gave 0·2061 CO_2 and 0·0548 H_2O. C $= 63·37$; H $= 6·88$.
$C_{14}H_{18}O_5$ requires C $= 63·2$; H $= 6·8$ per cent.

0·1200 required 18·62 c.c. of $Ba(OH)_2$ solution (0·0243N) for neutralisation. $C_{14}H_{18}O_5$ (monobasic) requires 18·6 c.c.

5-cyclo*Hexane*spiro*dicyclopentan*-3-on*e*-1 : 2-*dicarboxylic Acid* (XXII, p. 335).

The formation of this substance as a by-product in the preparation of the various acid-esters of the series has already been noticed. It was found to be produced in good yield by boiling either the yellow sodium compound or the acid-ester (XVIII, p. 334) with 10 parts by weight of 20 per cent. aqueous hydrochloric acid for twelve hours. As the boiling proceeded, oily products separated out, and subsequently passed again into solution. Then crystals appeared in the boiling liquid. At the end of the period, the mixture was cooled and allowed to remain at the ordinary temperature for twenty-four hours, after which practically the whole of the organic material had crystallised out. The crystalline mixture consisted of about three parts of the dibasic acid XXII to one part of the monobasic acid XXIII (p. 335). It was boiled with four times its weight of water, and the suspension cautiously cooled and quickly filtered. By this means, the monobasic acid was separated almost quantitatively from a solution which, in the cold, was supersaturated with respect to the dibasic acid. The agitation caused by filtering usually caused the filtrate to set to a stiff paste of crystals of the dibasic acid. These were recrystallised from water.

The acid separated from water in rosettes of long, silky, needle-shaped crystals, which melted and decomposed at 234°. It gave a deep crimson colour with ferric chloride, but did not appear to be acted on when boiled with hydrochloric acid for several days:

0·1087 gave 0·2407 CO_2 and 0·0584 H_2O. C = 60·39; H = 5·97.
    $C_{12}H_{14}O_5$ requires C = 60·5; H = 5·9 per cent.

0·0715 required 24·65 c.c. $Ba(OH)_2$ solution (0·0243N) for neutralisation. $C_{12}H_{14}O_5$ (dibasic) requires 24·7 c.c.

The *anhydride*, $C_5H_{12}{:}C\!<$ CO—O—CO, with the structure, was produced when the free acid was treated with acetyl chloride at 100° in a closed flask. The solid residue obtained on evaporation was triturated with aqueous sodium hydrogen carbonate and recrystallised from ether. It melted at 154°, and on treating with aqueous sodium hydroxide gave the sodium salt of the original dibasic acid:

0·1050 gave 0·2515 CO_2 and 0·0518 H_2O. C = 65·32; H = 5·48.
    $C_{12}H_{12}O_4$ requires C = 65·5; H = 5·5 per cent.

5-cyclo*Hexane*spiro*dicyclo*pentan-3-*one*-1-*carboxylic Acid* (XXIII, p. 335).

A mixture of about one part of this acid to three parts of the dibasic acid (XXII, p. 335) was formed when either the triethyl ester, XV, or its sodium compound, or the diethyl hydrogen ester, XVII, or its potassium compound, or the ethyl dihydrogen ester, XVIII, was boiled for twelve hours with 20 per cent. hydrochloric acid. The ethyl hydrogen ester XXI was found to be converted quantitatively into the monobasic acid by boiling hydrochloric acid. The dibasic acid XXII, on the other hand, did not appear to be affected by this reagent.

The dibasic acid, when heated above its melting point, however, evolved carbon dioxide, and from the dark-coloured residue a small amount of monobasic acid could be isolated. A good yield was obtained when the dibasic acid was heated with water at 200° for about ten minutes. The acid-esters XVII and XVIII also gave excellent yields of the monobasic acid when treated in this way. The triethyl ester XV, however, required the presence of a trace of acid in the water. A small quantity of hydrochloric acid or acetic acid, or even of butyric acid, was found to be sufficient.

The most convenient way of preparing the monobasic acid is by heating the yellow sodium compound with a slight excess of dilute hydrochloric acid at 200°. When preparing considerable quantities, however, it was found desirable to drive off as much carbon dioxide and alcohol as possible before closing the vessel. The

sodium compound, in portions of about 10 grams, was boiled with ten times its weight of 20 per cent. hydrochloric acid for twelve hours in a strong flask provided with a short reflux air-condenser. Enough aqueous sodium hydroxide was then added to reduce the concentration of free mineral acid to 2 or 3 per cent., and the solution was again boiled to expel the air. The flask was then securely corked and immersed in an oil-bath at 200° for ten minutes. After cooling to the ordinary temperature, the crystals were collected and recrystallised from 96 per cent. alcohol, using a little animal charcoal to remove the dark impurities. The yield was 85 per cent.

The monobasic acid was sparingly soluble in hot or cold water and in most cold organic solvents, but it crystallised well from hot ethyl alcohol in long needles. It melted at 236° without decomposition, and gave no colour with ferric chloride. It was found to be unacted on by boiling aqueous or alcoholic potassium hydroxide, and by prolonged boiling with hydrochloric acid. Cold alkaline permanganate was, however, instantly decolorised:

0·1337 gave 0·3310 CO_2 and 0·0860 H_2O. C=67·52; H=7·14.

$C_{11}H_{14}O_3$ requires C=68·0; H=7·2 per cent.

The *semicarbazone,* $C_5H_{10}{:}C{<}{C(CO_2H){\cdot}CH_2 \atop CH{-\!-\!-}C{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2}$ was prepared by boiling the acid with an aqueous solution of semicarbazide acetate for a few seconds. On cooling the solution, the semicarbazone separated out, and was recrystallised from alcohol. It melted and decomposed at 259°:

0·1071 gave 0·2240 CO_2 and 0·0661 H_2O. C=57·04; H=6·85.

$C_{12}H_{17}O_3N_3$ requires C=57·4; H=6·8 per cent.

trans-3-*Hydroxy*-4-cyclo*hexyl*cyclobutan-2-*one*-3 : 4-*dicarboxylic Acid* (XXIV, p. 336).

Five grams of the yellow sodium compound were boiled with 30 c.c. of 4N-alcoholic potassium hydroxide, the boiling being continued for one hour after the suspended matter had become colourless; or, alternatively, 5 grams of the acid-ester (XVIII, p. 334) were boiled with 30 c.c. of the same reagent for one hour. In either case, the product was isolated by evaporating the alcohol and adding water and hydrochloric acid. The acid solution was extracted ten times with its own volume of ether, and the extract dried over calcium chloride for at least three days. This was found to be necessary, since the acid was present in the ether in its hydrated form, which apparently gave up water to the calcium chloride very slowly, and incomplete dehydration interfered with

the subsequent purification. When quite dry, the ether was evaporated and the viscid residue triturated with chloroform. The crystals which were caused to separate by this treatment were drained on porous porcelain and washed with fresh ether.

The acid prepared in this way was fairly pure and melted and decomposed at 203°. It was very readily soluble in water and in all the usual organic solvents, except chloroform and light petroleum. In these solvents it was only sparingly soluble, but it did not appear to crystallise well from mixtures of solvents. It gave no colour with ferric chloride, and did not appear to be acted on by boiling acetyl chloride (compare Part I). The acid was purified for analysis through the hydrate (see below):

0·1331 gave 0·2734 CO_2 and 0·0748 H_2O. C=56·02; H=6·24.

$C_{12}H_{16}O_6$ requires C=56·2; H=6·2 per cent.

0·0352 required 11·25 c.c. $Ba(OH)_2$ solution ($0·0243N$) for neutralisation. $C_{12}H_{16}O_6$ (dibasic) requires 11·3 c.c.

The *hydrated* form, $C_{12}H_{16}O_6,2H_2O$, separated in large, dense prisms when the anhydrous acid was dissolved in hot water and the solution cooled. The hydrated acid readily dissolved in dry ether, and was much more readily soluble in chloroform than the anhydrous substance. At 100°, it evolved water vapour, leaving the anhydrous acid in a very pure form, melting at 206° to a colourless liquid, which evolved steam, and, after cooling, set to a solid mass, which melted at about 135°:

0·1648 lost 0·0201 at 100°. H_2O=12·20.

$C_{12}H_{16}O_6,2H_2O$ requires H_2O=12·3 per cent.

The *silver* salt was precipitated by silver nitrate from a neutral solution of the ammonium salt:

0·1435 gave 0·0656 Ag. Ag=45·71.

0·1729 ,, 0·1929 CO_2 and 0·0473 H_2O. C=30·43; H=3·03.

$C_{12}H_{14}O_6Ag_2$ requires C=30·6; H=3·0; Ag=45·9 per cent.

The *barium* salt was precipitated from a solution of the acid in water by adding an excess of barium hydroxide:

0·1007 gave 0·0595 $BaSO_4$. Ba=34·74.

$C_{12}H_{14}O_6Ba$ requires Ba=35·1 per cent.

cis-3-*Hydroxy*-4-cyclo*hexyl*cyclo*butan*-2-*one*-3 : 4-*dicarboxylic Acid* (XXIV, p. 336).

This acid was prepared by dissolving its anhydride (see below) in a slight excess of $4N$-aqueous sodium hydroxide and then adding a slight excess of concentrated hydrochloric acid. The precipitated acid was collected and dried. It was then dissolved in

P *

dry ether containing a trace of alcohol, and caused to crystallise from this solution by adding benzene. The crystals were finally purified by triturating with pure dry ether and again recrystallising from a mixture of ether and benzene containing alcohol.

The pure *cis*-acid melted at 145°, and rapidly evolved water vapour. It readily dissolved in water or alcohol, but was almost insoluble in pure dry ether. Unlike the *trans*-form, it did not appear to take up water of crystallisation:

0·0929 gave 0·1912 CO_2 and 0·0548 H_2O.   C$=56·13$; H$=6·55$.
$C_{12}H_{16}O_6$ requires C$=56·3$; H$=6·3$ per cent.
0·0446 required 14·40 c.c. $Ba(OH)_2$ solution (0·0243N) for neutralisation. $C_{12}H_{16}O_6$ (dibasic) requires 14·3 c.c.

The Anhydride of the cis-*Acid*, $C_5H_{10}{:}CH{\cdot}C{<}^{-CH_2-}_{C(OH)}{>}CO$
$\underset{\dot{C}O{\cdot}O{\cdot}\dot{C}O}{\diagup}$
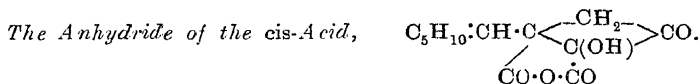
The *trans*-acid, on heating above its melting point, gave off water vapour. The transformation was, however, by no means complete unless the fused material was raised to 240—250° and maintained at this temperature until it began to darken in colour. The product solidified on cooling, and, after triturating with aqueous sodium hydrogen carbonate and drying, was recrystallised from dry ether. It separated in large, oblique prisms which melted at 155°. The substance was also recrystallised from benzene.

The same anhydride was obtained by heating the *cis*-acid above its melting point:

0·1335 gave 0·2959 CO_2 and 0·0709 H_2O.   C$=60·45$; H$=5·90$.
$C_{12}H_{14}O_5$ requires C$=60·5$; H$=5·9$ per cent.

The cis-*Anilic Acid*, $C_5H_{10}{:}CH{\cdot}C{<}^{-CH_2-}_{C(OH)}{>}CO$
$\overset{|}{\underset{CO{\cdot}NH{\cdot}C_6H_5}{CO_2H}}$
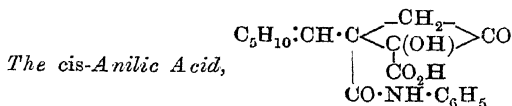
This substance was at once precipitated when the *cis*-anhydride was dissolved in benzene and treated with a solution of aniline in the same solvent. It was purified by first triturating with ether and then recrystallising from dilute alcohol. It separated in minute crystals, which melted and decomposed at 202°:

0·1145 gave 0·2721 CO_2 and 0·0666 H_2O.   C$=64·81$; H$=6·46$.
$C_{18}H_{21}O_5N$ requires C$=65·3$; H$=6·3$ per cent.

$$C_5H_{10}:CH\cdot C\!\!<^{-CH_2-}_{C(OH)}\!\!> CO$$

The cis-*Anil*, $\overset{\displaystyle|}{\underset{\displaystyle C_6H_5\cdot N\!-\!CO}{CO}}$.
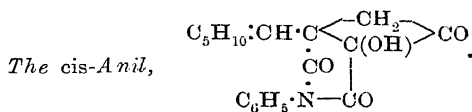
The *cis*-anil was readily obtained by heating the anilic acid at 210° until the evolution of steam had ceased. The product was triturated with sodium hydrogen carbonate and then recrystallised from absolute alcohol. It separated in long, silky needles which melted at 199°:

0·1098 gave 0·2778 CO_2 and 0·0592 H_2O.   C = 69·00 ; H = 5·99.

$C_{18}H_{19}O_4N$ requires C = 69·0 ; H = 6·1 per cent.

(e) *Comparative Experiments with the Acid-Esters* (XXVI, p. 337, *and* XVIII, p. 334) *of the Dimethyldicyclopentane and* cyclo*Hexane*spiro*dicyclopentane Series.**

One molecular proportion of each acid-ester was boiled for fifteen minutes with 6 molecular proportions of potassium hydroxide in 3·6N-solution in ethyl alcohol. The bulk of the alcohol was evaporated under diminished pressure and water and excess of hydrochloric acid were added to the residue. The acid products were then extracted quantitatively with ether.   The percentage yields were as follows :

TABLE VI.

Bridged-ring-acid-ester XXVI.			Bridged-*spiro*-acid-ester XVIII.		
Acid-ester recovered.	Monocarboxylic acid formed.	Fission product formed.	Acid-ester recovered.	Products of loss of 4-carbethoxyl group.	Fission products formed.
85	1·5	0	0	0	85
81	4	0	5	0	78

In all cases a small quantity of gummy material was formed, and for this reason the whole of the original material was never accounted for as crystalline products. The small quantity of monocarboxylic acid XIV was readily isolated by reason of its sparing solubility in cold water. The recovered acid-ester XVIII was also quite easily separated from the fission product by means of dry chloroform in which the latter, if quite anhydrous, is almost insoluble.

* See note, p. 337.

(f) *Preparation and Hydrolysis of the Methylation Product of the Yellow Sodium* spiro-*Compound* (XII, p. 330).

The yellow sodium compound does not react at all readily with methyl iodide under the usual conditions even at 100° in a closed flask. If, however, four or five times the theoretical quantity of methyl iodide is used, methylation proceeds rapidly.

Ethyl cyclo*Hexane*spiro-2-*methyldicyclopentan*-3-*one*-1 : 2 : 4-*tricarboxylate* (XXX, p. 342).

Twenty grams of the yellow sodium compound were heated with a solution of 20 grams of methyl iodide in 100 grams of absolute alcohol at 100° for one and a-half hours in a closed flask, which, from time to time, was vigorously shaken. The excess of the methyl iodide and most of the alcohol were then distilled off and the residue poured into 400 c.c. of water. The precipitated oil was extracted with ether, the extract being washed with water and sodium carbonate solution, dried, and evaporated. The oily residue was found to decompose on attempting to distil it under diminished pressure. It was therefore allowed to remain in an exhausted desiccator for several days and then analysed:

0·1109 gave 0·2556 CO_2 and 0·0729 H_2O. C = 62·86; H = 7·30.

$C_{20}H_{28}O_7$ requires C = 63·2; H = 7·4 per cent.

The figures quoted are those for one of three closely agreeing analyses. They indicate that a partial conversion into the methyl diethyl ester has taken place:

$C_{19}H_{26}O_7$ requires C = 62·2; H = 7·0 per cent.

This is perhaps a natural result of the use of a large excess of methyl iodide in the preparation.

trans-*Lactonic Acid of γ-Hydroxy-β-*cyclo*hexyl-α-methyltricarballylic Acid* (XXXIV, p. 342).

Twenty-five grams of the methylated ester were boiled under a reflux condenser with 170 c.c. of 4*N*-alcoholic potassium hydroxide for two and a-half hours. The mixture was then cooled and the precipitated salts were collected and drained on porous porcelain in a desiccator. They were then dissolved in water and the solution was acidified and repeatedly extracted with ether. The residue left after drying and evaporating the extract was caused to deposit crystals by triturating with benzene, the process being repeated until an ultimate gummy residue was obtained, from which no crystals would separate.

The crystals were placed in a test-tube with just sufficient benzene to cover them. The benzene was then boiled for a few minutes and the suspension filtered while hot. The filtrate on cooling deposited crystals of the lactonic acid.

The ultimate gummy residue was esterified with alcohol and sulphuric acid in the usual way, and, after adding water, the esters were extracted with ether. From the extract the acid products were shaken out with aqueous sodium hydroxide, and again extracted from the aqueous solution after acidification. The residue obtained on evaporating the ether was hydrolysed by boiling hydrochloric acid. After twelve hours the liquid was rendered alkaline and extracted with ether, then re-acidified, and again extracted with ether. On drying and evaporating the latter extract a residue was obtained which, when treated with benzene, yielded a further quantity of the crystalline lactonic acid.

The substance, after recrystallisation from benzene, melted at $172°$ without decomposition, and did not appear to decompose appreciably at $260°$. It dissolved very readily in water or alcohol, and fairly readily in benzene or chloroform:

0·1310 gave 0·2774 CO_2 and 0·0800 H_2O. $C = 57·75$; $H = 6·78$.
$C_{13}H_{18}O_6$ requires $C = 57·8$; $H = 6·7$ per cent.

The *silver* salt was at once precipitated when silver nitrate was added to a boiled solution of the lactonic acid in ammonia:

0·1118 gave 0·0449 Ag. $Ag = 44·63$.
$C_{13}H_{16}O_6Ag_2$ requires $Ag = 44·6$ per cent.

trans-γ-*Hydroxy*-β-cyclo*hexyl*-α-*methyltricarballylic Acid.*

The hydroxy-acid appeared to be stable only in the form of its salts, and in spite of several attempts it was not found possible to obtain it free. However, when the *trans*-lactonic acid was dissolved in water and slowly titrated with barium hydroxide an end-point corresponding with the neutralisation of three carboxyl groups was obtained:

0·0434 of the *trans*-lactonic acid required 19·90 c.c. $Ba(OH)_2$ solution ($0·0243N$) for complete neutralisation. $C_{13}H_{18}O_6$ changing in solution to $C_{13}H_{20}O_7$ (tribasic) requires 19·85 c.c.

The *barium* salt was prepared by treating a solution of the *trans*-lactonic acid in water with an excess of aqueous barium hydroxide:

0·1671 gave 0·1202 $BaSO_4$. $Ba = 42·34$.
$(C_{13}H_{17}O_7)_2Ba_3$ requires $Ba = 42·0$ per cent.

cis-*Lactonic Acid of γ-Hydroxy-β-cyclohexyl-α-methyltricarballylic Acid* (XXXIV, p. 342).

This substance was readily obtained by dissolving its anhydride (see below) in boiling sodium hydroxide solution, and acidifying with hydrochloric acid. Microscopic crystals separated and were recrystallised from water.

The *cis*-lactonic acid melted at 152° with the immediate elimination of water vapour. It was more readily soluble in water than the *trans*-acid:

0·1182 gave 0·2489 CO_2 and 0·0724 H_2O.   C = 57·43; H = 6·81.

$C_{13}H_{18}O_6$ requires C = 57·8; H = 6·7 per cent.

The *silver* salt was prepared by adding a solution of silver nitrate to a boiled solution of the *cis*-lactonic acid in ammonia:

0·1029 gave 0·0457 Ag.   Ag = 44·41.

$C_{13}H_{16}O_6Ag_2$ requires Ag = 44·6 per cent.

On boiling with concentrated hydrochloric acid the *cis*-lactonic acid was partly converted into the *trans*-isomeride.

cis-*γ-Hydroxy-β-cyclohexyl-α-methyltricarballylic Acid.*

Like the *trans*-modification, this substance appeared to be stable only in the form of its salts. The *cis*-lactonic acid on titration with aqueous barium hydroxide gave, however, an end-point corresponding with salt-formation in respect of three carboxyl groups:

0·0260 of the *cis*-lactonic acid required 11·9 c.c. $Ba(OH)_2$ solution (0·0243N) for complete neutralisation. $C_{13}H_{18}O_6$ changing in solution to $C_{13}H_{20}O_7$ (tribasic) requires 11·9 c.c.

The *barium* salt was precipitated from a solution of the *cis*-lactonic acid in water by the addition of an excess of barium hydroxide solution:

0·1403 gave 0·1011 $BaSO_4$.   Ba = 42·42.

$(C_{13}H_{17}O_7)_2Ba_3$ requires Ba = 42·0 per cent.

$$CO\text{--}O\text{--}CO$$
The cis-*Lactonic Anhydride,* $C_5H_{10}{:}CH{\cdot}C\text{-----}CH{\cdot}$
$$MeCH{\cdot}CO{\cdot}O$$
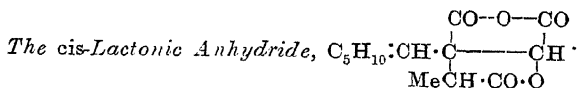
The lactonic anhydride was prepared by heating the *trans*-lactonic acid with acetyl chloride at 100° in a closed flask. The product was evaporated in a vacuum and the residue crystallised from ether,

when it separated in small crystals melting at 170°. It could also be purified by distillation under diminished pressure.

The same anhydride was also obtained by boiling the *cis*-lactonic acid with acetyl chloride at atmospheric pressure:

0·1170 gave 0·2637 CO_2 and 0·0679 H_2O. C = 61·47; H = 6·45.
$C_{13}H_{16}O_5$ requires C = 61·9; H = 6·3 per cent.

trans-3-*Hydroxy*-4-cyclo*hexyl*-1-*methyl*cyclo*butan*-2-*one*-3 : 4-*dicaroxylic Acid* (XXXVII, p. 345).

The portion of the crystalline mixture obtained in the preparation of the *trans*-lactonic acid (p. 369) which did not diissolve in the boiling benzene consisted essentially of the *cyclo*butane acid XXXVII, and was recrystallised from aqueous alcohol.

The ethereal solution of the esterified gummy residue (p. 369), after shaking out the acid products with aqueous sodium hydroxide, was dried and evaporated. The residue, on distillation under diminished pressure, yielded a fraction passing over at about 260°/25 mm., which was hydrolysed by boiling hydrochloric acid. The product was rendered alkaline and extracted with ether, then acidified, and again extracted with ether. The latter extract, on drying, and evaporating the solvent, yielded a residue which deposited crystals of the *cyclo*butane acid on adding benzene. The crystals were washed with benzene and recrystallised from aqueous alcohol.

The *trans-cyclo*butane acid melted and evolved steam at 185°, without appreciable discoloration. The liquid, on cooling, solidified, and on re-heating melted at about 140°:

0·1008 gave 0·2132 CO_2 and 0·0618 H_2O. C = 57·68; H = 6·81.
$C_{13}H_{18}O_6$ requires C = 57·8; H = 6·7 per cent.
0·0600 required 18·37 c.c. $Ba(OH)_2$ solution (0·0243N) for neutralisation. $C_{13}H_{18}O_6$ (dibasic) requires 18·3 c.c.

cis-3-*Hydroxy*-4-cyclo*hexyl*-1-*methyl*cyclo*butan*-2-*one*-3 : 4-*dicarboxylic Acid* (XXXVII, p. 345).

The *cis*-acid was prepared by boiling its anhydride (see below) with water. On cooling the solution the anhydride separated in the pure condition.

The acid melted at 148° with the immediate elimination of water-vapour. It was more readily soluble in water than the *trans*-modification:

0.0704 gave 0.1497 CO_2 and 0.0430 H_2O.   C = 57.99; H = 6.78.

$C_{13}H_{18}O_6$ requires C = 57.8; H = 6.7 per cent.

0.0481 required 14.65 c.c. $Ba(OH)_2$ solution (0.0243N) for neutralisation. $C_{13}H_{18}O_6$ (dibasic) requires 14.7 c.c.

When boiled for four hours with concentrated hydrochloric acid the *cis*-acid was quantitatively converted into the *trans*-isomeride.

Anhydride of the cis-*Acid,* $C_5H_{10}{:}CH{\cdot}C{<}^{CHMe}_{C(OH)}{>}CO.$ / $CO{\cdot}O{\cdot}CO$
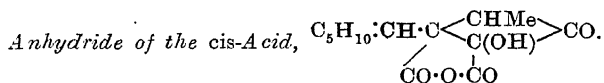
At its melting point the *trans*-acid evolved water-vapour, but the elimination was by no means complete at this temperature.   The melted substance was therefore raised to 230° and maintained at this temperature until it began to darken in colour.   The product was triturated with aqueous sodium hydrogen carbonate, dried, and recrystallised from dry ether.   It melted at 158°.

The same anhydride was obtained by heating the *cis*-acid above its melting point:

0.0833 gave 0.1886 CO_2 and 0.0483 H_2O.   C = 61.75; H = 6.44.

$C_{13}H_{16}O_5$ requires C = 61.9; H = 6.3 per cent.

(g) *Reduction of the Monobasic Bridged-*spiro-*acid* (XXIII, p. 335) *by Sodium Amalgam.*

It was found necessary, in order to be able to repeat the results, to standardise carefully the method of experiment.   The reductions were always carried out with 3 per cent. amalgam, which passed through a 10-mesh sieve but not through a 16-mesh sieve.   The solutions were contained in round-bottomed flasks of capacity two and a-half times the volume of the solution, and kept at a definite temperature.   During a reduction a stream of carbon dioxide was led into the flask, but was not allowed to bubble through the liquid. These conditions apply to all the experiments described in this and the next section.

5-cyclo*Hexane*spirocyclo*pentan-3-one-1-carboxylic Acid* (XLIII, p. 348).

Five grams of the ketonic acid (XXIII, p. 335) were dissolved in an amount of sodium carbonate sufficient to give a neutral solution and the whole made up to 200 c.c.   This solution was kept at 14° by immersing it in cold water and reduced under the standard

conditions by adding 10 grams of amalgam once every half hour until 120 grams in all had been used. Half an hour after the addition of the last of the amalgam the mercurial layer was removed and the aqueous layer acidified. The oily precipitate was allowed to solidify and was then collected and recrystallised from dilute alcohol.

The acid melted at 136—138°, and was found to be very readily soluble in all usual organic solvents except light petroleum; in this solvent, as in water, it was sparingly soluble:

0·0867 gave 0·2145 CO_2 and 0·0635 H_2O.   C=67·49; H=8·14.
$C_{11}H_{16}O_3$ requires C=67·3; H=8·2 per cent.

The Semicarbazone, $C_5H_{10}:C{<}\genfrac{}{}{0pt}{}{CH(CO_2H){\cdot}CH_2}{CH_2{-}\!\!-\!\!-\!\!-\!\!-C:N{\cdot}NH{\cdot}CO{\cdot}NH_2}$.
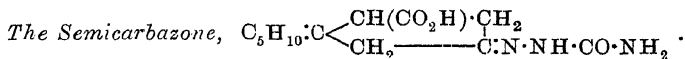
The semicarbazone separated when a solution in which the acid and semicarbazide acetate had been boiled together was cooled. After recrystallising from alcohol it melted and decomposed at 210°:

0·1079 gave 0·2262 CO_2 and 0·0757 H_2O.   C=57·17; H=7·80.
$C_{12}H_{19}O_3N_3$ requires C=56·9; H=7·5 per cent.

5-cycloHexanespirocyclopentan-3-ol-1-carboxylic Acid (XLIV, p. 348).

Five grams of the above *cyclo*pentanone acid were dissolved in a quantity of aqueous sodium carbonate sufficient to give an approximately neutral solution which was made up to 400 c.c. This solution was kept at 17° and reduced under standard conditions with 240 grams of amalgam, 10 grams being added every half hour. Half an hour after the addition of the last of the amalgam the mercurial layer was run off and the aqueous layer acidified and extracted with ether. The solid residue obtained after the ether had been dried and distilled off was recrystallised from a mixture of benzene and light petroleum.

The hydroxy-acid melted at 125—127° and was very readily soluble in all the usual organic solvents except light petroleum. It was much more readily soluble in water than was the corresponding ketonic acid:

0·1092 gave 0·2672 CO_2 and 0·0884 H_2O.   C=66·93; H=9·00.
$C_{11}H_{18}O_3$ requires C=66·7; H=9·1 per cent.

$$Acetyl\ Derivative,\ C_5H_{10}:C{<}{{CH(CO_2H)\cdot CH_2}\atop{CH_2\text{------}CH\cdot OAc}}$$
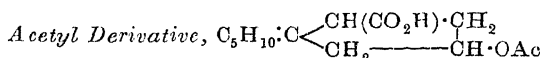
When the hydroxy-acid was boiled with acetyl chloride for four hours and the solution evaporated there was left a solid residue which was recrystallised from benzene. It melted at 157—160°:

0·0887 gave 0·2122 CO_2 and 0·0680 H_2O. C = 65·24; H = 8·52.

$C_{13}H_{20}O_4$ requires C = 65·0; H = 8·3 per cent.

0·1552 gave acetic acid requiring 26·4 c.c. $Ba(OH)_2$ solution (0·0243N) for neutralisation. $C_{13}H_{20}O_4$ requires 26·6 c.c.

(h) *Comparative Experiments on the Reduction of the Bridged-ring- and Bridged-spiro-acids XIV* (p. 333) *and XXIII* (p. 335).

The general plan which was followed in these experiments has already been sketched in the Introduction (Section E).

The most convenient method of preparing the bridged-ring acid XIV was found to be by treating the sodium compound IX (p. 330) according to the method (p. 364) used in the preparation of the acid XXIII from the sodium compound XII. The reductions of the bridged-ketonic-acids XIV and XXIII were carried out under the usual conditions (p. 372). The experiments were conducted in pairs, using 0·80 gram of the acid XIV and 1·00 gram of the acid XXIII. The neutral solutions of the acids were immersed in the same water-bath and treated with 1 gram of amalgam every fifteen minutes so long as the experiment lasted. The aqueous layers were then acidified and extracted quantitatively with pure ether. The solid residues obtained on evaporating the solvent were allowed to remain in an exhausted desiccator for forty-eight hours.

The dried products were then analysed. Usually about 0·4 or 0·5 gram was taken and the water formed by combustion determined. In certain cases the substance was also acetylated and the product left after evaporating, desiccated over potassium hydroxide and quantitatively hydrolysed, the acetic acid being distilled off in a current of steam and estimated by titration with standard alkali. This figure gave the quantity of hydroxy-acid which had been formed in the reduction, whilst the water formed on combustion enabled one to calculate the total quantity of hydrogen which had been introduced during the reduction. The accompanying table (table VII) gives the results of these experiments, the figures within the brackets (......) representing the calculated limits.

Another set of experiments, similar to the above, was instituted,

in which the reduced ketonic-acids XXXIX (p. 346) and XLIII (p. 348) were used in place of the bridged-ketonic-acids XIV and XXIII. The quantities taken for each experiment were 0·80 gram of the acid XXXIX, and 1·00 gram of the *spiro*-acid XLIII. The other quantities and conditions of experiment were the same as in the former case. In this instance the products were not acetylated and hydrolysed, but the water formed on combustion was determined. The results of these experiments are given in table VIII, the figures in brackets (......) representing, as before, the calculated limits.

TABLE VII.

Time (hours).	Amalgam (grams).	Bridged-ring-acid (0·80 gram).			Bridged-*spiro*-acid (1·00 gram).		
		Per ce of H produ	Atoms of H introduced.	Per cent. hydroxy acid.	Per cen of H i produc	Atoms of H introduce:d.	Per cent. hydroxy acid.
(0	0	6·49	0·00		7·22	0·00	0)
1	4	6·67	0·30		7·49	0·58	
2	8	6·85	0·60		7·64	0·89	
4	16	7·20	1·18		7·97	1·58	
6	24	7·27	1·30	0	8·09	1·85	2
10	40	7·46	1·62	3	8·30	2·30	18
14	56	7·79	2·16	21	—	—	—
(∞		8·86	4·00	100	9·09	4·00	100)

TABLE VIII.

Time (hours).	Amalgam (grams).	Ring-acid (0·80 gram).		*spiro*-Acid (1·00 gram).	
		Per cent. of H in product.	Atoms of H introduced.	Per cent. of H in product.	Atoms of H introduced
(0	0	7·69	0·00	8·16	0·00)
2	8	7·92	0·39	8·39	0·49
4	16	8·13	0·75	8·51	0·75
7	28	8·42	1·25	8·67	1·10
(∞	∞	8·86	2·00	9·09	2·00)

(i) *Oxidation of Fission-products Derived from the Bridged*-spiro-*sodio-ester XII* (p. 330).

Oxidation experiments were tried with three types of fission-product, including the *spirocyclo*pentanone acid XLIII (p. 348), the *transcyclo*hexylcyclobutane acid XXIV (p. 336), and the *trans*-lactonic acid of hydroxy*cyclo*hexylmethyltricarballylic acid XXXIV (p. 342). None of these appeared to be acted on by boiling dilute nitric acid. Concentrated nitric acid, however,

readily oxidised the first of these three acids, but did not react with the last two. These, however, were readily attacked by warm alkaline permanganate. Two crystalline oxidation products, *cyclo*hexanecarboxylic acid and *cyclo*hexane-1:1-dicarboxylic acid, were obtained in the course of these experiments.

cyclo*Hexane*-1:1-*dicarboxylic Acid* (XLV, p. 351).

This acid was prepared by oxidising both the *spirocyclo*pentanone acid XLIII (p. 348), or the corresponding *spirocyclo*pentanol acid XLIV (p. 348), with concentrated nitric acid. The organic acid (2·5 grams) was warmed with an excess of concentrated nitric acid until most of the red fumes had been evolved. The resulting solution was then boiled for a few minutes, and finally evaporated to dryness. The residue was treated with water and again evaporated. In this way, a semi-solid mass was obtained, from which the crystals were separated by spreading on porous porcelain.

After recrystallising from water, the acid melted at 207°, with the evolution of carbon dioxide and a certain amount of discoloration:

0·1008 gave 0·2058 CO_2 and 0·0650 H_2O.   C = 55·68; H = 7·16.
$C_8H_{12}O_4$ requires C = 55·8; H = 7·0 per cent.
0·0412 required 19·75 c.c. $Ba(OH)_2$ solution (0·0243N) for neutralisation. $C_8H_{12}O_4$ (dibasic) requires 19·7 c.c.

cyclo*Hexanecarboxylic Acid* (*Hexahydrobenzoic Acid*).

This acid was obtained in two ways:

(1) *By distilling* cyclo*hexane*-1:1-*dicarboxylic acid*. The dicarboxylic acid on distillation under ordinary pressure gave off carbon dioxide and yielded a distillate, which boiled at 230—235° and solidified when cooled by ice. The crystals melted at 18—23°. (Found: C = 65·42; H = 9·51. Calc.: C = 65·6; H = 9·4 per cent.)

(2) *By oxidising* cyclo*hexyl derivatives*. Either the *trans*-lactonic acid of hydroxy*cyclo*hexylmethyltricarballylic acid XXXIV (p. 342) or the *trans-cyclo*hexyl*cyclo*butanone acid XXIV (p. 336) may be used. The organic acid (10 grams) was dissolved in an excess of a solution of sodium carbonate and treated with 30 grams of potassium permanganate. The permanganate was added in successive small quantities, sufficient time being allowed between each addition for the solution to become decolorised, the reaction being aided by heating. When all the permanganate had

been added and decolorised, the liquid was filtered and extracted with ether to remove any neutral oxidation products. The aqueous solution was then acidified with hydrochloric acid, and the acid products were extracted with ether. From the residue obtained on drying and evaporating the solvent, some gummy material was separated by distilling under diminished pressure, and the liquid distillate was fractionally distilled under atmospheric pressure. In this way, there was obtained a fraction boiling at 232—236°, which solidified on cooling in ice to a mass of crystals melting at 21—25°. (Found: $C = 65.63$; $H = 9.51$. Calc.: $C = 65.6$; $H = 9.4$ per cent.)

The acid prepared by both these methods melted at a temperature a few degrees lower than the recorded melting point, namely, 29° (Lumsden, T., 1905, **87**, 91). The same experience in regard to it is recorded by Haworth and Perkin (T., 1894, **65**, 103). It certainly appears to be exceedingly difficult to obtain preparations showing the correct melting point when working with small quantities of material. Crystals of the acid when left exposed to air rapidly liquefied, and it did not appear to be possible to induce the acid to separate in a crystalline form by cooling a solution in light petroleum below 0°. These observations agree precisely with the statements made by Lumsden, and, along with the analytical figures, are regarded as leaving no doubt as to the identity of the substance.

(j) *Examination of the Oily By-product obtained in the Preparation of the Bridged-spiro-sodio-ester XII* (p. 330).

The alcoholic solution of the oily by-product obtained during the preparation of the yellow sodium spiro-compound (p. 357) was distilled to remove the alcohol, the residue dissolved in ether and shaken with water. The ethereal solution was then dried and evaporated, the residue being distilled under diminished pressure. Three fractions were obtained: (1) below 120°/20 mm., (2) between this and 250°/11 mm., and (3) at 250—160°/11 mm., together with a small, dark-coloured, non-volatile residue.

Fraction (1).—The first fraction contained practically the whole of the ethyl malonate present in the original oil. It was redistilled, and the small residue of high boiling point was added to the second fraction, (2).

Fraction (2).—The second fraction, which did not appear to be capable of separation into pure compounds by distillation, was boiled with hydrochloric acid for forty-eight hours. During the reaction, a strong odour of butyric acid was developed. When

the hydrolysis was complete, the butyric acid was distilled off in a current of steam, and the residual solution boiled with charcoal, filtered, and evaporated to dryness. Five acids were isolated from the crystalline residue.

cyclo*Hexane*-1 : 1-*diacetic Acid.*—The crystalline residue was recrystallised from the minimal quantity of 35 per cent. alcohol. The crystals which separated contained three of the five acids, the separation from the other two, which remained in the mother liquor, being very nearly quantitative. The crystals melted at 160—200° approximately. They were dissolved in dilute ammonia and, after the excess of ammonia had been evaporated, were treated in the cold with a solution of zinc sulphate. The precipitate was collected, washed with cold water, and then digested with hydrochloric acid. The acid thus precipitated melted at 174—179°, and was again precipitated as its zinc salt. The free acid was then liberated and recrystallised from water, when it melted at 181°, and was identified as *cyclo*hexane-1 : 1-dicarboxylic acid by direct comparison with a specimen of that substance. The preparation, together with some small residues obtained subsequently, constituted 15 per cent. of the original crystalline mixture.

trans-cyclo*Hexane*spirocyclo*propane*-1 : 2-*dicarboxylic Acid.*

The combined filtrates from the zinc salt of *cyclo*hexane-1 : 1-diacetic acid were concentrated and treated with concentrated hydrochloric acid. The precipitated acids were dissolved in ammonia, and, after concentrating the solution, treated in the cold with a considerable excess of a saturated solution of lead nitrate. The lead salts were collected and recrystallised from the minimal quantity of boiling water, and then decomposed with a slight excess of dilute nitric acid. This treatment separated the last trace of *cyclo*hexanediacetic acid, which, along with a small quantity of the *trans-spirocyclo*propane acid, remained in the filtrates from the lead salt. These traces were separated by means of their zinc salts, as described above. The combined *cyclo*hexanediacetic acid-free preparations were extracted twice with three parts by weight of boiling benzene. The undissolved portion melted at 234—237°, and on recrystallisation from dilute alcohol melted sharply at 237°. It was identified as *cyclo*hexane*spirocyclo*propanedicarboxylic acid by direct comparison with a specimen. The preparation, together with some residues subsequently obtained, amounted to 65 per cent. of the original crystalline mixture.

3-cyclo*Hexane*spiro-1-*methyl*cyclopropane-1 : 1′ : 2-*tricarboxylic Acid* (XLVII, p. 354).

The solution in the 35 per cent. alcohol from which the above two dicarboxylic acids were crystallised (p. 378) was evaporated, and the residue resolved by crystallisation from 50 per cent. alcohol into three distinct fractions: (1) a small quantity of a mixture of the same two dicarboxylic acids, (2) a much more readily soluble, crystalline substance melting at about 208°, and (3) a viscous gum.

The first fraction was treated according to the methods already described for the separation of the two dicarboxylic acids.

The second consisted essentially of the *spirocyclo*propanetricarboxylic acid. It represented about 8 per cent. of the original crystalline mixture, and, on recrystallising from water, melted at 215°, with the immediate elimination of water vapour:

0·1156 gave 0·2386 CO_2 and 0·0675 H_2O. C = 56·30; H = 6·49.
$C_{12}H_{16}O_6$ requires C = 56·2; H = 6·2 per cent.
0·0453 required 21·95 c.c. $Ba(OH)_2$ solution (0·0243N) for neutralisation. $C_{12}H_{16}O_6$ (tribasic) requires 21·9 c.c.

$$\text{The Anhydro-acid, } C_5H_{10}{:}C{<}^{\overset{\displaystyle CO\cdot O\cdot CO}{\underset{\displaystyle CH_2}{|}}}_{CH\cdot CO_2H} \quad \text{or} \quad C_5H_{10}{:}C{<}^{\overset{\displaystyle C\text{---}CO}{|}}_{\underset{\displaystyle CH\cdot CO}{|}}{>}O.$$
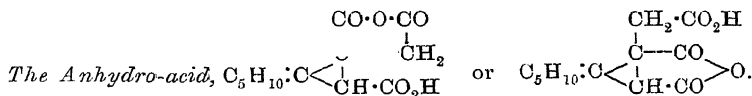
The anhydro-acid was prepared by boiling the free tricarboxylic acid with acetyl chloride for two hours and evaporating the excess of the reagent. The residue on treating with benzene set to a mass of crystals. After recrystallising from the same solvent, the anhydro-acid melted at 128°. It was immediately soluble in cold sodium hydrogen carbonate solution, and could be recovered unchanged by acidifying. On boiling a solution of the anhydro-acid in aqueous sodium hydroxide for a few minutes and then acidifying, the free tribasic acid was regenerated:

0·1548 gave 0·3418 CO_2 and 0·0823 H_2O. C = 60·23; H = 5·90.
$C_{12}H_{14}O_5$ requires C = 60·5; H = 5·9 per cent.

5-cyclo*Hexane*spiro-2-*ethyldi*cyclopentan-3-*one*-1-*carboxylic Acid.* (XLVIII, p. 354).

The two benzene filtrates obtained in the preparation of the *spirocyclo*propanedicarboxylic acid (p. 378) were combined and evaporated. The residue, which still contained about three parts

of the dicarboxylic acid to one of the bridged-monocarboxylic acid
(this was indicated by a titration), was weighed, and extracted
with three times its weight of boiling benzene. The extract was
evaporated and the residue treated again in this way, the treat-
ment being repeated until the residue obtained after evaporating
an extract was completely soluble in three parts of boiling benzene.
The product was fractionally crystallised from benzene. After a
considerable number of fractional crystallisations, a preparation
was obtained which did not appear to change in melting point
when again recrystallised.

This substance separated from benzene in long needles, which
melted at 191—194°. It was sparingly soluble in water and gave
no colour with ferric chloride:

0·0610 gave 0·1537 CO_2 and 0·0432 H_2O. C = 69·75; H = 7·99.
$C_{13}H_{18}O_3$ requires C = 70·3; H = 8·1 per cent.

0·0376 required 7·20 c.c. $Ba(OH)_2$ solution (0·0243N) for
neutralisation. $C_{13}H_{18}O_3$ (monobasic) requires 7·0 c.c.

The analytical figures, especially those for the titration, do not
correspond with the formula so well as could be desired. The dis-
crepancies are, however, all in a direction that may be taken to
indicate that the preparation still contained a small quantity of
the *spirocyclo*propanedicarboxylic acid, which, owing to the small-
ness of the quantity of material, it was not possible to remove.
The preparation constituted about 0·1 per cent. of the original
crystalline mixture.

trans-*Lactonic Acid of* γ-*Hydroxy*-β-cyclo*hexyl*-α-*ethyltricarballylic
Acid* (XLIX, p. 354).

The viscous gum, which was obtained as the third fraction in
the separation by means of 50 per cent. alcohol mentioned on
p. 379, was distilled under diminished pressure. More than three-
quarters of it passed over at 240—250°/40 mm., and this, on
treatment with benzene, solidified to a mass of colourless crystals.
These represented about 3 per cent. of the original crystalline
mixture, the residue in the distilling flask, which was not further
examined, accounting for about 1 per cent.

The crystalline lactonic acid, after recrystallisation from either
water or benzene, melted at 149°. It dissolved readily in water
and all the usual organic solvents except light petroleum:

0·1228 gave 0·2660 CO_2 and 0·0962 H_2O. C = 59·08; H = 7·09.
$C_{14}H_{20}O_6$ requires C = 59·2; H = 7·0 per cent.

The *silver* salt was precipitated by adding silver nitrate solution
to a boiled solution of the lactonic acid in ammonia:

0·1063 gave 0·0461 Ag. Ag = 43·37.

$C_{14}H_{18}O_6Ag_2$ requires $Ag = 43·4$ per cent.

trans-γ-*Hydroxy-β-cyclohexyl-α-ethyltricarballylic Acid.*

This hydroxy-acid (contrast the *cis*-form) appeared to be stable only in the form of its salts. All attempts to obtain it in the free state were unsuccessful. However, when the *trans*-lactonic acid was dissolved in water and the solution titrated slowly with barium hydroxide in the cold, an end-point corresponding with the neutralisation of three carboxyl groups was obtained :

0·0516 required 22·40 c.c. $Ba(OH)_2$ solution $(0·0243N)$ for complete neutralisation. $C_{14}H_{20}O_6$, changing in solution to $C_{14}H_{22}O_7$ (tribasic), requires 22·4 c.c.

The *barium* salt was precipitated from an aqueous solution of the *trans*-lactonic acid by adding an excess of a solution of barium hydroxide :

0·1678 gave 0·1179 $BaSO_4$. $Ba = 41·36$.

$(C_{14}H_{19}O_7)_2Ba_3$ requires $Ba = 40·8$ per cent.

cis-*Lactonic Acid of γ-Hydroxy-β-cyclohexyl-α-ethyltricarballylic Acid* (XLIX, p. 354).

The *cis*-lactonic acid was readily prepared by heating the free *cis*-hydroxy-acid (see below) at 100° for a few minutes.

When dissolved in water the lactonic acid regenerated the hydroxy-acid, which could either be crystallised out or titrated in solution. The lactonic acid could, however, be recrystallised from a mixture of benzene and light petroleum without any change taking place. It melted at 198° with the evolution of water-vapour :

0·1040 gave 0·2244 CO_2 and 0·0664 H_2O. $C = 58·84$; $H = 7·10$.

$C_{14}H_{20}O_6$ requires $C = 59·2$; $H = 7·0$ per cent.

The *silver* salt was prepared by dissolving either the *cis*-lactonic acid or the *cis*-hydroxy-acid (see below) in dilute ammonia, boiling, and adding an excess of silver nitrate solution :

0·1041 gave 0·0449 Ag. $Ag = 43·13$.

$C_{14}H_{18}O_6Ag_2$ requires $Ag = 43·4$ per cent.

On boiling the *cis*-lactonic acid with hydrochloric acid a partial conversion into the *trans*-lactonic acid took place.

cis-γ-Hydroxy-β-cyclohexyl-α-ethyltricarballylic Acid.

This substance was prepared by boiling the *cis*-lactonic anhydride (see below) with a slight excess of aqueous sodium hydroxide and acidifying with hydrochloric acid. The *cis*-hydroxy-acid slowly separated out.

The substance is very unstable, and loses a molecule of water with great readiness, giving the *cis*-lactonic acid. The change was found to proceed with rapidity at 60° in an exhausted desiccator at the ordinary temperature, and slowly when the acid was exposed to air under ordinary conditions. In cold aqueous solution the substance behaved in every way as a tribasic acid :

0·1003 gave 0·2045 CO_2 and 0·0666 H_2O. C = 55·60 ; H = 7·38.
$C_{14}H_{22}O_7$ requires C = 55·6 ; H = 7·3 per cent.

0·0382 required 16·65 c.c. $Ba(OH)_2$ solution (0·0243N) for neutralisation. $C_{14}H_{22}O_7$ requires (tribasic) 16·6 c.c.

The *barium* salt was precipitated when the hydroxy-acid was dissolved in water and treated with an excess of barium hydroxide solution :

0·1057 gave 0·0740 $BaSO_4$. Ba = 41·18.
$(C_{14}H_{19}O_7)_2Ba_3$ requires Ba = 40·8 per cent.

When the *cis*-hydroxy-acid was boiled with 20 per cent. hydrochloric acid for some hours a partial conversion into the *trans*-lactonic acid took place.

$$\text{The cis-Lactonic Anhydride, } C_5H_{10}{:}CH{\cdot}C\begin{matrix}CO{-}O{-}CO\\|\qquad\qquad|\\ \qquad\qquad CH\\ Et{\cdot}CH{\cdot}CO{\cdot}O\end{matrix}$$
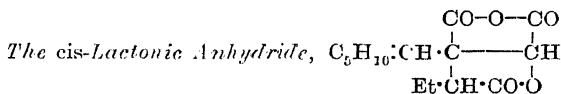
The *trans*-lactonic acid did not appear to be dehydrated to any appreciable extent when heated above its melting point or when distilled under diminished pressure. It readily eliminated water, however, when heated at 100° for half an hour with acetyl chloride. On evaporating the product and treating the residue with benzene, crystals of the lactonic anhydride were obtained. After being recrystallised from benzene the substance melted at 154°. It did not dissolve at an appreciable rate in cold aqueous sodium hydrogen carbonate, but on warming with sodium hydroxide both oxygen rings were opened up and the *cis*-hydroxy-acid was formed :

0·1023 gave 0·2356 CO_2 and 0·0625 H_2O. C = 62·81 ; H = 6·79.
$C_{14}H_{18}O_5$ requires C = 63·2 ; H = 6·7 per cent.

Fraction (3).—The third fraction which was obtained on distilling

the oily by-product (p. 377) boiled at 250—260°/11 mm. and consisted of fairly pure ethyl *cyclo*hexane*spiro*methyl*cyclo*propanetetra-carboxylate (XI, p. 330). When hydrolysed with hydrochloric acid it yielded the tricarboxylic acid (XLVII, p. 354) dealt with on p. 379.

(k) *Note on Ethyl Dihydrogen* 5:5-*Dimethyldicyclopentan-3-one-*
1:2:4-*tricarboxylate* (XXVI, p. 337).

This member of the dimethyldi*cyclo*pentane series, which was made use of in this research, has not been previously described.

The yellow sodium compound X (p. 330) was boiled with five times its weight of a 3N-solution of potassium hydroxide in alcohol until the suspended matter just became colourless. The precipitate was collected and drained on porous porcelain in a desiccator. It was then dissolved in the minimal quantity of water and decomposed with excess of concentrated hydrochloric acid. The crystals obtained were recrystallised from 15 per cent. hydrochloric acid.

The acid-ester melted and decomposed at 162°, and gave a purple colour with ferric chloride. It was readily converted into the monocarboxylic acid XIV (p. 333) by heating for a few minutes at 200° with a little water. When heated in the dry state, it evolved carbon dioxide and steam, and from the charred residue a small amount of the acid XIV was isolated. It is perhaps worthy of note that the monocarboxylic acid should be obtained in this way, but it is doubtless the result of the hydrolytic action of the steam which is evolved as the substance decomposes:

0·1261 gave 0·2453 CO_2 and 0·0599 H_2O. C=53·05; H=5·28.

$C_{12}H_{14}O_7$ requires C=53·3; H=5·2 per cent.

0·1070 required 32·7 c.c. $Ba(OH)_2$ solution (0·0243N) for neutralisation. $C_{12}H_{14}O_7$ (dibasic) requires 32·6 c.c.

IMPERIAL COLLEGE OF SCIENCE
AND TECHNOLOGY,
SOUTH KENSINGTON.

RESEARCH LABORATORIES,
CASSEL CYANIDE COMPANY, LTD.,
GLASGOW.

ANNUAL GENERAL MEETING,

THURSDAY, MARCH 27TH, 1919, AT 4 P.M.

SIR WILLIAM J. POPE, K.B.E., F.R.S., President, in the Chair.

Dr. T. S. PRICE and Dr. C. K. TINKLER were elected Scrutators, and the ballot was opened for the election of Officers and Council.

The Report of Council for 1917–1918 was formally presented to the meeting by the PRESIDENT. After statements by one of the Secretaries as to the progress made in the revision of the Bye-laws and by the Treasurer as to the financial position of the Society, the adoption of the Report of Council, together with the Statement of Accounts for the year ending December 31st, 1918, was proposed by Professor G. BARGER, seconded by Dr. G. W. MONIER-WILLIAMS, and carried unanimously.

REPORT OF COUNCIL, 1918–1919.

The Council are gratified to report a substantial increase in the membership of the Society. On December 31st, 1917, the number of Fellows was 3,270. During 1918, 249 Fellows were elected and 13 reinstated, making a gross total of 3,532. The Society has lost 62 Fellows by death; 16 have resigned; the elections of 6 have been declared void, and 47 have been removed for non-payment of Annual Subscriptions. The total number of Fellows, therefore, as at December 31st, 1918, was 3,401, showing an increase of 131, as compared with 72 in 1917.

It is with regret they report that the following Fellows have died on Service:

John Percy Bates (1913).   Edward Frank Harrison (1894).
Charles William Dick (1917). Leonard Ison Pitt (1911).

and that the death of the following has also occurred :

Richard Leburn Barnes (1875).
James Bayne (1874).
William Henry Blake (1890).
Arthur Clegg Bowdler (1865).
Joseph John Bowley (1896).
Harry Broadbent (1889).
William Edward Callister (1909).
Thomas Charles Cloud (1878).
James Mason Crafts (1870).
William Adam Dixon (1862).
John Ernest Dunstan (1917).
Thomas Farries (1870).
Charles Thomas Foreman (1907).
Edward Francis (1879).
Charles James Pemeller Fuller (1896).
George Thomas Glover (1872).
Walter Augustus Handcock (1900).
Egerton Hargreaves (1909).
Henry James Helm (1872).
Richard Pendarves Hodges (1913).
Henry Tylston Hodgson (1873).
William Lamond Howie (1876).
Edward Lewis James (1912).
David Smith Jardin (1902).
Edgar Dingle Jones (1912).
John Sydney Keel (1917).
Douglas Rayment Keller (1913).
William Joel Kemp (1882).
Hassum Alidina Lakhani (1909).
Edmund Albert Letts (1879).

Thomas Stratford Logan (1902).
Thomas Watson Lovibond (1882).
Sydney Lupton (1872).
George Cannon McMurtry (1889).
Charles Stewart Maries (1918).
Edward Matthey (1884).
Elias Mendoza (1918).
Alexander Milne (1885).
Sir Alexander Pedler (1870).
Mulgrave Daniel Penney (1870).
George Frederick Tyler Phillips (1904).
William Ping (1889).
Joseph Price Remington (1886).
Alfred Gordon Salamon (1880).
John Scudamore Sellon (1875).
Alfred Senier (1875).
Walter Dalrymple Severn (1896).
John William Shepherd (1899).
Richard Spencer (1886).
James Carter Spensley (1917).
Henry Charles Stephens (1880).
Edward Cumming Thompson (1894).
John Bishop Tingle (1889).
Thomas Tyrer (1876).
Herbert William Mills Willett (1906).
Christopher Wilson (1894).
Reginald Cowdell Woodcock (1871).
John Young (1874).

Resignations have been received from :

William James Bees (1905).
Hugh Garner Bennett (1909).
Kula Bhushan Bhaduri (1903).
Frederick Raine Ennos (1914).
Nagardas Purushottam Gandhi (1915).
John Thomas Hall (1903).
Herbert Edwin Macadam (1896).
David James Morgan (1895).

Frederick Filmer de Morgan (1897).
Joseph Morris (1891).
Malur Srinivasa Rau (1910).
Abhayacharan Sanyal (1891).
Robert Greig Smith (1891).
Thomas May Smith (1910).
Alfred Tingle (1904).
James Woodward (1888).

The congratulations of the Society are offered to Professor William Odling, Past-President, elected a Fellow on January 17th, 1848, who has now completed seventy-one years as a Fellow. The Society's congratulations are also extended to :

	Elected.
Dr. Augustus George Vernon Harcourt (Past-President)......	Feb. 3rd, 1859.
John Spiller	Feb. 3rd, 1859.
Josiah Wyckliffe Kynaston..:..	Feb. 17th, 1859.
Thomas William Salter..	Feb. 17th, 1859.

who have been Fellows for more than sixty years, and to the
following, who have attained their jubilee as Fellows:

	Elected.
John Hughes	Dec. 17th, 1868.
Edward Knowles Muspratt	Jan. 21st, 1869.
Thomas Bolas	Mar. 18th, 1869.
Frank Clowes	Mar. 18th, 1869.

The volume of Transactions for 1918 contains 995 pages, of
which 849 pages are occupied by 89 memoirs, the remaining 146
pages being devoted to the Obituary Notices, three lectures on
special subjects, the Report of the Annual General Meeting, and
the Presidential Address. The volume for the preceding year con-
tained 95 memoirs occupying 960 pages. The Journal for 1918
contains also 2,436 abstracts occupying 1,032 pages, whilst the
abstracts for 1917 numbered 2,858 and occupied 1,308 pages. The
great decrease in the number of memoirs in journals devoted to
chemistry and allied subjects referred to in the Reports for 1916
and 1917 became, as was expected, still more marked in 1918;
there is, however, some slight reason to hope that the lowest point
has been reached, and that an increase in the number of papers
abstracted may now be anticipated. Whilst most of the Continental
journals have been obtained for abstraction, no Russian journals
have come to hand during the year.

In the last Report, an account was given of the arrangements
made by a Joint Committee of the Chemical Society and Society
of Chemical Industry to minimise duplication in the abstracts pub-
lished in the Journals of the two Societies. This arrangement has
been in force during the year with satisfactory results.

The abstracts may be classified as follows:

PART I.

	Pages.	No. of Abstracts.
Organic Chemistry	—	771
Physiological Chemistry	—	237
Chemistry of Vegetable Physiology and Agriculture	—	160
	564	1,168

PART II.

General and Physical Chemistry	—	557
Inorganic Chemistry	—	205
Mineralogical Chemistry	—	59
Analytical Chemistry	—	447
	468	1,268
Total in Parts I. and II	1,032	2,436

The scheme for supplying the abstracts of the Chemical Society and of the Society of Chemical Industry to the members of both Societies has been further considered, but owing to many difficulties arising out of the war, such as the greatly increased cost of production, it has been postponed for the present.

The Report on the progress of Radioactivity for 1917, which was omitted from the last volume of Annual Reports, is included with that for 1918 in the current Volume XV; it has been decided to postpone the Report on Crystallography and Mineralogy for 1918 and to combine this with the Report for 1919. Permission has been given for the publication of a French translation of Volume XV of the Annual Reports.

The publication of the List of Fellows has been resumed, but, owing to the need for economy, the list has been issued only to those Fellows who made application.

Following the scheme initiated three years ago, arrangements have been made for the delivery of Lectures to the Society during the present session. The first, entitled "The conception of the chemical element as enlarged by the study of radioactive change," was given by Professor F. Soddy on December 19th; on March 6th a lecture on "Emission spectra and atomic structure" was delivered by Professor Nicholson, whilst Professor Jeans will give a lecture on May 1st dealing with "The quantum theory and new theories of atomic structure."

The address delivered by the President at the last Annual Meeting was, by order of the Council, widely circulated throughout the country. The emphasis laid in this address on the desirability of closer co-operation between the societies representing the various branches of chemistry has given rise to a definite step in this direction by the promotion of "The Federal Council for Pure and Applied Chemistry." The Federal Council consists of representatives appointed by the following eleven societies: the Chemical Society, the Society of Chemical Industry, the Association of British Chemical Manufacturers, the Institute of Chemistry, the Society of Public Analysts, the Faraday Society, the Biochemical Society, the Iron and Steel Institute, the Institute of Brewing, the Society of Dyers and Colourists, and the Society of Glass Technology. The delegates elected by the Council to represent the Society on this body are Professor H. E. Armstrong, Sir William J. Pope, and Sir William A. Tilden. The primary objects of the new body are to consider and act upon all matters involving the common interests of the constituent societies and to deal with any question which these may place before it. The provision of a House adequate to the requirements of the chemical profession, in

which a complete scientific and technical Library could be assembled, is now under the consideration of the Federal Council.

The Council have had under consideration the present conditions of chemical research, and they have given particular attention to the question of the adequacy of the sums available for grants and to the restricted supply of pure chemicals. Since it appeared desirable that united action should be taken in these matters, the Federal Council. has been requested to consider them, and has already taken action in both directions.

The demobilisation of chemists has also had the earnest attention of the Council, and joint representation with the Royal Society, the Institute of Chemistry, and the Chemical Warfare Department has been made to the proper authorities.

The Council have recently received a valuable report from the General Committee of Chemical and Allied Societies on the proposed publication of chemical compendia in the English language. The report has also been placed before the Federal Council and the councils of other interested societies, including those of the American and French Chemical Societies, with the view of securing their co-operation.

During the past year a Committee has been appointed to consider what changes it is desirable to make in the Bye-laws of the Society. In their report, the Committee have recommended considerable changes, but these are in several respects inconsistent with the terms of the present Charter, and therefore cannot be made until a supplemental Charter has been obtained. The question whether application for a supplemental Charter should be made will shortly be laid before an Extraordinary General Meeting.

Sir William A. Tilden represented the Society on the Sectional Committee of the British Scientific Products Exhibition.

Professor P. F. Frankland and Dr. A. Scott continue to act as the Society's representatives on the Conjoint Board of Scientific Societies, whilst Sir William J. Pope has been appointed a delegate to the International Association of Chemical Societies in place of the late Sir William Ramsay.

The Council are glad to report that, as a result of the Conference of Chemical and Allied Societies, a scheme has been prepared and is now in operation for increasing the use of the Library and extending its technical equipment. The co-operation and financial assistance of the Association of British Chemical Manufacturers, the Biochemical Society, the Faraday Society, the Institute of Chemistry, the Society of Chemical Industry, the Society of Dyers and Colourists, and the Society of Public Analysts have been obtained. The members of these societies are now able to use the

Library on the same terms as Fellows, and their representatives have been added to the Library Committee.

As already announced, the Library is now open to 9 p.m. on Tuesdays and Fridays and to 5 o'clock on Saturdays, in addition to those evenings on which the Society meets.

The number of books borrowed from the Library during 1918 was 2,005, as against 2,157 in the previous year and 1,610 in 1916. The additions to the Library comprise 126 books, 255 volumes of periodicals, and 31 pamphlets, compared with 155 books, 282 volumes of periodicals, and 54 pamphlets in 1917.

The Council have the pleasure to report that a valuable gift of handsomely bound volumes of periodicals and systematic works has been received as a bequest from the late Mr. Sydney Lupton.

The accounts for the year 1918 show a balance of income over expenditure amounting to £2,489 4s. 4d., as against £1,652 9s. 11d. reported last March for the previous year. Whilst the income from all sources has been £10,082 14s. 11d., and is thus greater than that recorded for 1917 by £1,552 16s. 0d., the expenditure has exceeded that of 1917 by £716 1s. 7d., reaching the sum of £7,593 10s. 7d. Thus, although the increased expenditure exceeds the similar increase on the outlay for 1916, indicated by the Report of last year, it has been amply covered by the larger revenue.

The latter factor is composed of additional life compositions, £102, and admission fees, £352, whilst the subscriptions account reveals an improvement by £381 10s. 0d. To these are added increases of £89 12s. 7d. from interest on investments, £262 9s. 10d. from the sale of publications, and £92 15s. 11d. from advertisements in the Journal, although the net gain to the Society from this source is only £32 5s. 4d., owing to increased cost of printing. Donations to the Library amounting to £280 5s. 0d., and not having a corresponding reference in the Report for 1917, cannot properly be regarded as increased revenue, as more than this sum will be expended by the Society during the current year in augmenting the usefulness of the Library to members of the subscribing bodies.

As was anticipated from the conditions prevailing during 1918, expenses in producing the various publications have been greater than the corresponding costs for 1917, the total increase being £390 19s. 7d., of which £128 5s. 2d. is due to the list of Fellows, a publication suspended in 1917. The fact that this compilation cost £73 1s. 6d. in 1914, £73 6s. 7d. in 1915, and £73 16s. 4d. in 1916 throws an interesting light on the increase in printing charges and on the period of the War at which this became acute.

Administrative expenditure has also increased from £1,472 4s. 5d.

to £1,681 6s. 5d., the principal items on this account being
£161 14s. 10d. in staff salaries and war bonus, whilst miscellaneous
printing, stationery, and postages have together increased by
£85 18s. 8d. On the other hand, the exceptional outlay in library
furniture required in 1917 has not been repeated, and is reflected
in a saving of £61 9s. 9d. in the year under review.

The War has continued to affect the volume of Transactions and
Abstracts, as indicated by the following synopsis:

					Number of Pages.		
					Trans.	Abstr.	Total.
1914	...	...	...	...	2,909	2,068	4,977
1915	...	...	...	...	1,862	1,944	3,806
1916	...	...	...	...	1,368	1,532	2,900
1917	...	...	...	...	1,128	1,308	2,436
1918	...	...	...	...	995	1,032	2,027

Nevertheless, the cost of printing the Journal has been
£2,750 8s. 3d., instead of £2,543 7s. 9d. in 1917, so that a reduc-
tion of 409 pages corresponds to an increase of £207 0s. 6d. in
expenditure; this is owing to further appreciation in the cost of
paper and to the necessity of raising the bonus paid to the printers,
which now stands at 72½ per cent. on the pre-war rates.

£2,000 National War Bonds were purchased during the year, and
the estimated value of the Society's other investments has improved
by £414, so that, having regard to the fact that on December 31st,
1918, the cash account was about £420 higher than on the last day
of 1917, the assets of the Society show an increase of £2,834, or a
total increase of £3,640 if the Research Fund at its present
estimated value is included.

The following grants have been made from the Research Fund
during the year:

	£	s.	d.
Organic derivatives of bismuth. F. Challenger.	£15	0	0
An investigation of the phthalein series. M. Copisarow. ...	10	0	0
The velocity of reaction between the alkyl iodides and sodium methoxide. H. E. Cox.	10	0	0
Formation of heterocyclic ring systems by the condensation of chlorocarbamic esters and alcohols. R. L. Datta. ...	10	0	0
The action of alcohols on urea nitrate. P. K. Dutt. ...	5	0	0
Influence of the nitro-group on the mobility of the sub-stituents in the benzene nucleus. J. Kenner. ...	5	0	0
The composition and structure of soaps. J. W. McBain. ...	15	0	0
Melting points of the substituted amides of the normal fatty acids. P. W. Robertson.	6	6	0
Synthesis of β-phenyl-β-hydroxymethylethylamine from cin-namic acid or ethyl cinnamate. E. H. Todd.	10	0	0
The space formulæ of diphenyl and its derivatives (con-tinued). E. E. Turner.	10	0	0
Total	£96	6	0

BALANCE SHEET.—THE CHEMICAL SOCIETY, 31ST DECEMBER, 1918.

Liabilities.

	£	s.	d.	£	s.	d.
To Subscriptions received in advance	234	0	0			
	1	10	0	235	10	0
Sundry Creditors				841	6	
Research Fund :—						
As per last Balance Sheet	14357	3				
Add Excess of Income over Expenditure for the year	539	18		14896	17	1
Chemical Society : Excess of Assets over Liabilities :—						
As per last Balance Sheet...	24768					
Add Excess of Income over Expenditure for the year	2189			27247	11	9

Assets.

	£	s.	d.	£	s.	d.
By Investments (value when acquired) :—						
£6730 Metropolitan Consolidated 3½ per cent. Stock	7212	8	6			
£1050 London and North Western Railway 3 per cent. Debenture Stock	839	12	6			
£1520 14s. 8d. Cardiff Corporation 3 per cent. Stock	1650	0	0			
£3400 India 3½ per cent. Stock	1816	1	0			
£2400 Bristol Corporation 2½ per cent. Debenture Stock	2070	2	5			
£4841 Midland Railway 2½ per cent. Preference Stock	3572	2	5			
£1200 Leeds Corporation 3 per cent. Debenture Stock	1143	1	0			
£1500 Transvaal 3 per cent. Guaranteed Stock,1923/53	1466	13	6			
£1900 North British Railway 3 per cent. Debenture Stock	1033	11	0			
£700 Canada 3½ per cent. Stock, 1930/50	704	8	6			
£2100 5 per cent. War Stock	5040	0	2			
£3100 5 per cent. War Bonds }						
(Estimated present value of Investments, £19,246 14s. 5d.)				2604·2	0	1
Sundry Debtors				1094	1	1
Subscriptions in Arrear Estimated to realise... ...				460	0	0
Insurance paid in advance				58	2	1
Cash at Bank—Deposit Account	300	0	0			
Current Account	353	9	0			
Cash in hand	16	14	10			
Research Fund :—						
Investments (value when acquired) :						
£1000 North British Railway 4 per cent. No. 1 Preference Stock	1010	0	0			
£4400 Metropolitan Consolidated 3½ per cent. Stock	4587	18	0			
£1084 Great Western Railway 2½ per cent. Debenture Stock	1049	15	11			
£1142 16s. New South Wales 3 per cent. Stock	1000	0	0			
£1122 Metropolitan Water Board 3 per cent. "B" Stock	1002	16	9			
£1365 Midland Railway 2½ per cent. Debenture Stock	1010	0	6			
£806 Victoria 3 per cent. Stock	705	6	9			
£498 11s. 0d. 5 per cent. War Stock	4267	4	10			
(Estimated present value of Research Fund Investments, £12,013 16s. 8d.)						
Cash at Bank...				670	3	10
				14634	2	
				£48,321	4	2

I have examined the above Balance Sheet and accompanying Income and Expenditure Accounts with the Books and Vouchers of the Society, and certify them to be in accordance therewith. I have also verified the Balance at the Bankers and the Investments.

W. B. KEEN,
Chartered Accountant.

Approved—C. F. CROSS.
GEORGE SENTER,
ARTHUR R. LING.

23, QUEEN VICTORIA STREET, E.C,
March 5th, 1919.

INCOME AND EXPENDITURE ACCOUNT

Income.

	£	s.	d.	£	s.	d.
To Life Compositions				349	0	0
,, Admission Fees				956	0	0
,, Annual Subscriptions—						
Received in advance, on account of 1918	139	3	4			
,, during 1918 ,, ,, ...	4729	16	8			
,, ,, ,, ,, 1917	392	0	0			
,, ,, ,, ,, 1916 and previous	62	0	0			
	5323	0	0			
Less amount included in last year's Income, being valuation of						
Arrears as per last Balance Sheet	400	0	0			
	4923	0	0			
Add Arrears at date : 1918, £670 ; 1917 and previous, £524, estimated						
to realise as per Balance Sheet	460	0	0			
				5383	0	0
., Lady Subscribers						
Investments :—						
Dividends on £6730 Metropolitan Consolidated 3½ per cent. Stock ...	170	15	8			
,, £1050 London and North Western Railway 3 per cent.						
Debenture Stock	23	4	7			
,, £1520 14s. 3d. Cardiff Corporation 3 per cent. Stock ...	33	1	6			
,, £1400 India 2½ per cent. Stock	25	7	6			
,, £2400 Bristol Corporation 2¼ per cent. Debenture Stock	42	0	0			
,, £4341 Midland Railway 2½ per cent. Preference Stock	79	7	2			
,, £1200 Leeds Corporation 3 per cent. Debenture Stock...	26	2	0			
,, £1500 Transvaal 3 per cent. Guaranteed Stock, 1923/53	31	10	0			
,, £1200 North British Railway 3 per cent. Debenture						
Stock	25	18	1			
,, £700 Canada 3½ per cent. Stock 1930/50	20	6	0			
,, £5200 5 per cent. War Stock and War Bonds...	205	8	3			
,, Income Tax Recovered	170	0	1			
,, Interest on Deposit Account	27	7	2			
				880	8	0
,, Publication Sales :—						
Journals	1728	6	0			
Proceedings	2	4	6			
Collective Index	33	17	2			
Library Catalogue	1	1	9			
Atomic Weight Tables		10	6			
Annual Reports on Progress of Chemistry	245	9	6			
Memorial Lectures	3	1	1			
Jubilee Volumes	0	17	6			
	2015	8	0			
Less Publishers' Commission	194	12	11			
				1820	15	
,, Proceeds of Advertisements in Journal...	£403	8	0			
Less Commission	29	8	4			
				373	19	8
,, Miscellaneous Receipts				8	6	2
,, Subscriptions from other Societies				22	1	0
Donations to Library				280	5	0
				£10,082	14	11

FOR THE YEAR ENDED 31ST DECEMBER, 1918.

Expenditure.

	£	s.	d.	£	s.	d.
B) **Expenses on account of Journal :—**						
Salary of Editor, including Indexing	620	0	0			
Salary of Sub-Editor and Assistant	250	0	0			
Editorial Postages	21	18	5			
Abstractors' Fees	240	12	1			
Printing of Journal	2750	8	3			
Banding	82	2	6			
Printing of Advertisements	164	13	2			
Wrappers and Addressing	4	5	4			
Distribution of Journal	398	19	4			
Authors' Copies	111	11	1			
Insurance of Stock	14	11	8			
				4659	1	10
,, Annual Reports on the Progress of Chemistry				460	4	9
,, Purchase of back numbers of Journal				6	4	3
,, List of Fellows				128	5	2
,, **Library Expenses :—**						
Salary of Librarian and Assistant...	371	17	0			
Books and Periodicals	199	1	8			
Binding	42	4	6			
				613	3	2
,, Indexing for International Catalogue				30	0	0
,, Donation to International Commission of Publication of Annual Tables of Constants and Numerical Data, Chemical, Physical and Techno-logical				10	0	0
,, Donation to Board of Scientific Societies...				5	5	0
,, **Administrative Expenses :—**						
Salary of Staff	539	15	0			
War Bonus	254	6	7			
Wages (Commissionaire, Housekeeper, and Charwoman)	215	19	0			
Coal and Lighting	61	18	1			
House Expenses and Repairs	87	2	4			
Furniture	8	3	0			
Tea Expenses	35	3	3			
Insurances	39	6	6			
Accountants' Charges	21	0	0			
Commission on Recovery of Income Tax	8	10	0			
Law Costs	10	10	0			
Miscellaneous Printing	129	4	6			
Stationery	129	17	4			
Postages	105	19	8			
Miscellaneous Expenses	34	11	2			
				1681	6	5
Balance, being excess of Income over Expenditure carried to Balance Sheet				2489	4	4

£10,082 14 11

RESEARCH FUND INCOME AND EXPENDITURE ACCOUNT FOR THE YEAR ENDED 31ST DECEMBER, 1918.

Income.

	£ s. d.	£ s. d.
To Dividends on:—		
£1000 North British Railway 4 per cent. No. 1 Preference Stock	29 10 6	
£4400 Metropolitan Consolidated 3½ per cent. Stock ...	111 13 0	
£1094 Great Western Railway 2½ per cent. Debenture Stock	10 1 3	
£1142 16s. New South Wales 3 per cent. Stock...	24 17 2	
£1122 Metropolitan Water Board 3 per cent. "B" Stock	24 11 5	
£1865 Midland Railway 2½ per cent. Debenture Stock ...	25 3 4	
£806 Victoria 3 per cent. Stock	17 10 7	
£4498 11s. 0d. 5 per cent. War Loan	217 0 0	
		469 7 3
" Repayment of Cost of Apparatus		7 12 0
" Repayments of Research Grants		81 10 1
" Income Tax Recovered		106 19 11
		£665 9 3

Expenditure.

	£ s. d.
By Grants	96 6 0
" Bankers' Charges	2 2 6
" Commission on Recovery of Income Tax	5 7 0
" Advertisements	2 0 0
" Longstaff Medal	2 0 0
" Do. do. Grant to Medallist ...	20 0 0
" Balance, being excess of Income over Expenditure, carried to Balance Sheet	539 13 9
	£665 9 3

Although one disbursement (£10) only was made in 1917, the balance of income over expenditure for 1918 is £539 13*s.* 9*d.*, as against £553 2*s.* 0*d.* for the previous year. This is explained by an increase of £50 11*s.* 3*d.* in the proceeds from investments, of £20 8*s.* 3*d.* in repayments of research grants, and of £14 0*s.* 3*d.* in the amount of income-tax recovered. £816 19*s.* 9*d.* Five Per Cent. War Loan was purchased for this account during 1918.

A vote of thanks to the Auditors proposed by the TREASURER was seconded by Mr. R. G. DURRANT, Dr. G. SENTER making acknowledgment.

On the motion of Mr. W. BARLOW, seconded by Mr. W. F. REID, a vote of thanks was proposed to the Treasurer, Secretaries, Foreign Secretary, and Council for their services during the past year. Acknowledgment was made by Dr. F. L. PYMAN.

The ballot was then declared closed.

The PRESIDENT delivered his Address, entitled "Chemistry in the National Service." A vote of thanks to the President for his services in the Chair and for his Address, coupled with the request that he would allow the Address to be printed in the Transactions, was moved by Professor H. E. ARMSTRONG. Col. C. T. HEYCOCK seconded the motion, which was carried with acclamation, the PRESIDENT making brief acknowledgment.

The report of the Scrutators was presented, and the PRESIDENT announced that the following had been elected as Officers and Council for the ensuing year:

President.—Sir James Johnston Dobbie, M.A., D.Sc., F.R.S.

Vice-Presidents who have filled the Office of President.—Henry Edward Armstrong, Ph.D., LL.D., F.R.S.; Alexander Crum Brown, D.Sc., LL.D., F.R.S.; Sir William Crookes, O.M., D.Sc., F.R.S.; Sir James Dewar, M.A., LL.D., F.R.S.; Harold Baily Dixon, C.B.E., M.A., Ph.D., F.R.S.; Percy Faraday Frankland, Ph.D., LL.D., F.R.S.; Augustus George Vernon Harcourt, M.A., D.C.L., F.R.S.; William Odling, M.A., M.B., F.R.S.; William Henry Perkin, Sc.D., LL.D., F.R.S.; Sir William Jackson Pope, K.B.E., M.A., D.Sc., F.R.S.; James Emerson· Reynolds, Sc.D., M.D., F.R.S.; Alexander Scott, M.A., D.Sc., F.R.S.; Sir Edward Thorpe, C.B., LL.D., F.R.S.; Sir William Augustus Tilden, D.Sc., LL.D., F.R.S.

Vice-Presidents.—Frederick George Donnan, M.A., Ph.D., F.R.S.; Henry John Horstman Fenton, M.A., Sc.D., F.R.S.; Arthur Smithells, C.M.G., F.R.S.; James Walker, D.Sc., LL.D., F.R.S.; William Palmer Wynne, D.Sc., F.R.S.; Sydney Young, D.Sc., F.R.S.

Treasurer.—Martin Onslow Forster, D.Sc., Ph.D., F.R.S.

Secretaries.—Samuel Smiles, O.B.E., D.Sc., F.R.S.; James Charles Philip, O.B.E., M.A., D.Sc., Ph.D.

Foreign Secretary.—Arthur William Crossley, C.M.G., D.Sc., F.R.S.

Ordinary Members of Council.—Julian Levett Baker; Alexander Findlay, M.A., D.Sc., Ph.D.; Francis Ernest Francis, D.Sc., Ph.D.; John Addyman Gardner, M.A.; Arthur Harden, D.Sc., Ph.D., F.R.S.; Thomas Anderson Henry, D.Sc.; Charles Alexander Hill, B.Sc.; James Colquhoun Irvine, D.Sc., Ph.D., F.R.S.; Charles Alexander Keane, D.Sc., Ph.D.; Robert Howson Pickard, D.Sc., Ph.D., F.R.S.; Sir Robert Robertson, K.B.E., M.A., D.Sc., F.R.S.; Edward William Voelcker.

PRESIDENTIAL ADDRESS.

Delivered at the ANNUAL GENERAL MEETING, March 27th, 1919.

By SIR WILLIAM J. POPE, K.B.E., F.R.S.

Chemistry in the National Service.

SINCE the autumn of 1914 a great change has taken place in the public attitude towards the natural sciences, and towards chemistry in particular. One of the recognised duties of the spokesmen of science during the past sixty years or more has been that of endeavouring to bring home to the general public and to its administrators the danger of neglecting the cultivation of pure and applied science. The eloquent discourses of our predecessors, Lyon Playfair, Roscoe, Meldola, and the veterans happily still with us, Tilden and Armstrong, all past-presidents of our society, on the national importance of chemistry, are well known to all of us, but we cannot claim that these utterances produced an effect compatible with their gravity.

Recent events have, however, given a stimulus to the popular appreciation of the need for wider application to scientific investigation of all kinds, which is incomparably greater than had been excited by the previous half-century of the spoken and written word. It may be useful at the present time to consider a few of the causes for this change in public opinion, partly because of the clarification of ideas which emerges from free discussion, partly because of the desirability of recording certain facts and particulars which may be of value to future historians of the strenuous period now ending and giving place to another still more strenuous.

At this time four years ago an urgent call was made for the services in a military capacity of all the chemists who could be spared from civil life. Large numbers were taken into the Army and formed the nucleus of the magnificent Gas Warfare Service, which has been slowly but efficiently developed. Many of these colleagues of ours are now returning to their legitimate spheres in the industrial and scientific life of the Empire, but many will not return; among those who have fallen I would refer more particularly to one who is well known to most of us present for the

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invaluable services which he rendered on the defensive side of chemical warfare. Lieut.-Colonel Harrison was one of the great discoveries of the War, and his death on the eve of the armistice was one of its many great tragedies; the protection against gas poisoning which has been employed by our own and allied troops, a protection far more efficient than that ensured by the devices elaborated at leisure by the Central Powers, was due mainly to his wide knowledge, great organising ability, and unfailing resourcefulness in emergency. A movement for the establishment of a memorial to Colonel Harrison was set on foot by the Chemical Warfare Committee, of which he was the Controller at the time of his death, and a considerable sum has been collected from those who had been associated with him in his work for the Services. The Chemical Warfare Committee have approached the Council of the Chemical Society, and have offered under certain conditions to place a memorial tablet or other suitable permanent memorial in these rooms, and also to establish, under certain further conditions, a trust fund to be held by the Society. The Council have with great pleasure intimated their willingness to accept these gifts, and one of the first duties of your new Council will be to decide how best to carry out the provisions of the trust deed.

The efficiency of the British gas protection, which called for the exhibition of so much scientific skill both in research and in manufacture, and led to its adoption by our Allies, is one striking illustration of the paramount importance of science which has appealed to the general public. This subject is, however, but a small branch of the enormous chemical problem which presented itself to the nation nearly five years ago and led to the organisation under Lord Moulton of the Department of Explosives Supplies. During the working out of this problem, issues presented themselves which are probably dissimilar from any that have ever arisen before.

Thus, as the magnitude of the struggle became gradually obvious, it was realised that the whole of the resources of the Empire would have to be utilised fully if success was to be attained. A census of all available chemical products had to be taken, and schemes for their exploitation laid down; all materials had to be apportioned out in accordance with the principle that whatever was used for the manufacture of one particular war material left a corresponding shortage of raw material in connexion with the manufacture of some other, and perhaps equally essential, product. The intricacy of gauging the chlorine output of the country, of determining how to increase it at the maximum rate without unduly disturbing other interests, of apportioning it

most advantageously for use as liquid chlorine and for the manu-
facture of phosgene, sulphur chloride, carbon tetrachloride, bleach-
ing powder, and many other war materials, is such as would dis-
arm criticism even if the result had been failure instead of brilliant
success.   This novel mode of presentment, involving recognition of
the principle that the Empire could only dispose of certain limited
and measurable quantities of raw materials, was but one of many
fresh views which forced themselves upon a newly created Minis-
terial Department.   Labour, fuel, and transport had to be discussed
in an analogous manner.

The cessation of hostilities found this country manufacturing,
roughly, 100,000 tons per annum of nitric acid and sulphur tri-
oxide, with an efficiency of about 93 and 91 per cent. respectively
of that theoretically obtainable; we were also making 60,000 tons
of T.N.T. and 35,000 tons of cordite per annum.   These produc-
tions were for all practical purposes on a permanent basis, and
could have been continued indefinitely.   The factories necessary
for securing this huge production were erected by the Government,
and for several reasons.   First, for economy in production.   In spite
of the large initial cost of installation, and including rapid amortisa-
tion, the national production of cordite was better in quality than,
and of approximately one-half the cost of, that imported from
America.   Secondly, for certainty of supply, which could be
ensured only by a home production not subject to the risks of over-
sea transport.

With this necessity for gigantic production, the urgency for
economy in manufacture necessarily went hand in hand.   One of
the most interesting documents of the war is the second report on
costs and efficiencies for H.M. factories controlled by the Depart-
ment of Explosives Supplies, which has been recently issued.   This
report contains a minute analysis of the working costs for each
period of each factory engaged on individual items of manufacture;
it states what proportion of the cost per ton of product is borne by
labour, raw materials, fuel, maintenance, etc., and provides an
incitement to further effort towards economy of working by giving
a "bogey" cost sheet made up of the most efficient details of cost
selected from the complete analysis of expenses.   It will be clear
that an immense amount of organising power was required to
achieve this stupendous result; it was due largely to the genius
and energy of Mr. K. B. Quinan.

It must be remembered, however, that this permanent memorial
to British chemical activity in production was rendered possible
only by the intense effort of the army of chemists and engineers
enlisted under the command of Lord Moulton.   The necessity for

utilising all the chemical resources of the country to the utmost led, in direct relationship with the census of raw materials previously mentioned, to the attempt to extract the last possible fraction of efficiency in each component process.   The huge production just indicated made it very profitable to carry out a vast amount of careful scientific investigation of details of manufacture; so many Fellows of this Society devoted their best efforts to this work that it would be invidious to mention names.   Our colleagues have had ample opportunity to realise that the romance of war is now to be found in the laboratory, the workshop, and the factory quite as much as on the battlefield.

An instructive example of the operations of the struggle for economy in the production of a given effect is found in the rivalry which arose between picric acid and ammonium nitrate for use as high explosives.   Picric acid costs about £185 per ton to make, ammonium nitrate about £50, and T.N.T. about £100 per ton; the high cost of picric acid means, of course, limited production.   A mixture of 80 parts of ammonium nitrate with 20 parts of T.N.T., known as amatol, was introduced early by the Research Department at Woolwich, as being about 5 per cent. more powerful as a high explosive, less "brisant," and more difficult to detonate, and, of course, far less costly to manufacture.   The course of the war has been marked by continued progress at the hands of our research chemists in the preparation and applications of amatol; the growing appreciation of the merits of this material led to the discontinuance of the manufacture of picric acid in this country last summer, to the adoption of amatol in place of picric acid as the American standard high explosive, to the approaching elimination of picric acid from the Italian military programme, and to the replacement, in the main, of picric acid by amatol in the French service.

A very pertinent question arises in connexion with the fact that our production of the chemical materials needed for a great European war was negligibly small in 1914 and has gradually attained satisfactory dimensions.   We know that the great chemical factories of Central Europe could divert their peace production of chemical products to a war output at very short notice.   None of these huge installations requires much time for the design and construction of chemical plant for new purposes; all possess a series of standard items of equipment which can be fitted together rapidly to form a piece of plant capable of use for throwing any ordinary laboratory operation into large-scale practice.   Stills, condensers, pressure vessels, filter presses, cooling arrangements of coils and

the like, are available in standard sizes and with standard fittings in such a manner that the installation on a works scale of a laboratory operation is deprived of its most formidable difficulties.   The question which demands an answer is why, when the German works were in existence and could attain a war production so quickly, were the Allied nations given time to gradually develop their war production of explosives, noxious materials, etc., from nothing? The question is best answered by an example.

In July, 1917, the Germans first used against the Allies a new offensive material, $\beta\beta$-dichloroethyl sulphide, $(CH_2Cl\cdot CH_2)_2S$, and with very great success.   This substance, the so-called "mustard gas," has but little odour, and exposure to it causes comparatively few fatalities; inhalation of, or contact with, its vapour gives rise to acute pneumonia, to the production of painful sores, and to temporary or even permanent blindness.   Whilst, as has been stated, the actual mortality is low, and the use of the substance may to this extent be described as humane, the casualties produced are very numerous; slight exposure to a material so toxic and so difficult to detect leads, in general, to six weeks in hospital.   The preparation of $\beta\beta$-dichloroethyl sulphide was described by Victor Meyer in 1886, and involved the several operations indicated by the following set of equations:

(1) $CH_2\!:\!CH_2 + HClO = CH_2Cl\cdot CH_2\cdot OH$.
(2) $2CH_2Cl\cdot CH_2\cdot OH + Na_2S = (HO\cdot CH_2\cdot CH_2)_2S + 2NaCl$.
(3) $(HO\cdot CH_2\cdot CH_2)_2S + 2HCl = (CH_2Cl\cdot CH_2)_2S + 2H_2O$.

When it is realised that operation No. 1 is difficult and that the products of reactions (1) and (2) are soluble in water, it will be understood that no small difficulties must present themselves in the manufacture of $\beta\beta$-dichloroethyl sulphide by this process on a large scale.   The examination of the German product made it quite clear, however, that the process of manufacture adopted was that indicated by the above set of equations; the over-all yield of product is perhaps 40 to 60 per cent. of the theoretical.   In view of the difficulties of manufacture, it was fairly certain that no chemical installation for its production could be established under the control of the Allies within any reasonable time; the Central Nations thus supposed that they held the monopoly of a very powerful instrument of war.

Most British organic chemists were, I think, amazed at the method of production adopted by the German manufacturers; to apply such a technically cumbrous process for the manufacture of so simple a compound seemed quite irrational.   By the end of

January, 1918, a process for making $\beta\beta$-dichloroethyl sulphide had
been worked out in the British laboratories, which consisted of the
reaction expressed by the following equation :

$$2CH_2\!:\!CH_2 + S_2Cl_2 = (CH_2Cl\cdot CH_2)_2S + S\,;$$
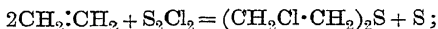
the yield obtained in the laboratory was 98 to 99 per cent. of that
theoretically possible.   The new method was communicated to
France and America, and installed by the three Great Allies on
a large scale; at the conclusion of the armistice the available daily
production of mustard gas by the Allies was equal to the monthly
production of the Central Nations.

The answer to the question just put is now available.   The
German chemical service was inefficient; the scientific chemists
under its control were incompetent.

The Allied production of mustard gas had a potentiality of the
order of thirty times as great as that of the German; the cost of
the German material was of the order of thirty times as great as
that of our product.   Cost of production under the conditions pre-
vailing for this particular material means, in the end, expenditure
in labour; that we were able to produce at something of the order
of one-thirtieth of the cost of the German production means that
by the allocation of the same quantity of raw materials we could
secure thirty times the output.   The relative strain on the pro-
ductive resources of the Allies and the Central Nations caused
by a demand for a certain quantity of "mustard gas" is measured
roughly by the indicated ratio of one to thirty.

Whilst many instances similar to that of mustard gas might be
quoted to show that Germany has been badly served by her scien-
tific men during the war, it would be difficult to overrate the effects
of the skill and perseverance exhibited by the German chemical
manufacturer.   The command ' of great and long-established
factories for fine chemical manufacture enabled the German
technologist to throw faulty academic projects rapidly into large-
scale production ; the cost, namely, the strain on national resources,
was enormous, but that an output could have been achieved is a
significant tribute to the potentialities represented by the large
German fine chemical factories.   Both in Britain and Germany
production in chemical manufacture has been multiplied during
the war, but necessarily in a different manner.   Our large produc-
tion is almost entirely of war importance, and most of the works
installed during the war must now be dismantled as a result of the
cessation of hostilities; the German expansions, on the other hand,
constitute a permanent addition to the potentialities of peace manu-
facture of staple marketable products.   The war has left Germany

with vastly increased resources as a manufacturer of much needed chemical products.

The view that our country is superior to Germany in the possession of creative scientific power has always been maintained in modern times by students of philosophy and history; the correctness of the view has been amply demonstrated during the last four years. Whilst our nation has overcome its initial handicap by a continuous flow of novel scientific devices of military value, our enemies passed through the war with little more in the shape of novel effects than those laboriously elaborated during the preceding years of peace. The more brilliant position which Germany has so long held in applied science arose from the keen appreciation exhibited by German public and official authorities of the rich economic fruits to be reaped from the systematic exploitation of scientific industry as compared with the neglect of scientific effort shown by corresponding classes in this country. Even yet, but small encouragement exists for those who desire to see pure and applied science flourish as it deserves in Great Britain; although it may be long before the scientific industries of Central Europe regain their former predominance, there seems but little prospect of sufficient official encouragement being given in this country to scientific and industrial initiative to ensure our position in the competition with other nations.

In this connexion it is interesting to notice what is happening in the United States. Immediately after her entry into the war America initiated a census of chemists, and in July, 1917, a fully detailed description was available of some 15,000 chemists resident in the States; a research staff consisting of 1200 technical men with appropriate assistance was enlisted for the Research Division of the Chemical Warfare Service alone. Since America was only in the war for about eighteen months this powerful organisation had not time to make its efforts properly felt. Apart from small improvements or changes in detail, practically all the American chemical equipment, both for offence and defence, was manufactured on the detailed plans furnished by Great Britain or France; the available time was too short to allow full play to American genius for novelty and for magnitude of production. The necessity for co-operation brought large numbers of young and active American chemical officers to Europe; it gave those officers for eighteen months the entry to practically every chemical works of importance in England and France, and unrivalled opportunities for accurately judging European chemical methods and markets. These men have now returned to their ordinary scientific and technical pursuits in the States, and it cannot be expected that they have left behind them

the unique experience which they have gained of European conditions.

We may anticipate that competition in pure and applied chemistry between Europe and America will become increasingly keener during the years to come. The competition is already intense, and gives little promise as yet of turning in our favour; it is, in fact, difficult to see how many of the staple products of fine chemical manufacture can hold their own in Great Britain against American competition under the conditions which arose during the first three years of the war. During these years peace production flourished in the States free from Government control, whilst in this country the establishment of a fine chemical industry in war time was naturally rendered far more difficult by State control of works, materials, and labour. The bearing of this may be made clear by an instance. The manufacture of "saccharin" was installed in England after the outbreak of war, but the production was controlled in that the manufacturers were only permitted to sell at a profit of 10 per cent. on the cost, this profit being, in turn, subject to the excess profits tax; further, to prevent the economic difficulties which were foreseen if "saccharin" competed with sugar, the price of English-made "saccharin" was fixed at a figure which involved the very large addition of thirty shillings per pound to the price, this addition being appropriated by the Government. Simultaneously, "saccharin" was manufactured free of all control in the States; it came into this country unrestricted and on such terms that the American producer took the thirty shillings per pound just mentioned in addition to the considerable profit previously made by reason of lower cost of manufacture. America having thus been assisted by our Government to build up a large reserve of profits, is now actually selling "saccharin" in England at eleven shillings per pound—a price at which it cannot be produced here—apparently with the legitimate trade purpose of destroying the English manufacture and subsequently running up the price.

Many cases may be quoted as closely analogous to that of "saccharin," notably in connexion with acetic acid, glycerol, acetone, and methyl alcohol and their products, in which British procedure has facilitated profiteering in foreign countries during the war. The excess profits tax operated insidiously in tempting British manufacturers to keep prices high so as to retain a margin with which to write off capital expenditure in spite of the tax; the foreign competitor, free from Government control of raw materials and exempt from the excess profits tax, was able to take full advantage of the ruling high rates. It will be of interest to see how the problems introduced by these actual occurrences are to be solved advantage-

ously for Great Britain in the great reconstruction upon which our administrators are now engaged.

Sufficient has probably now been said in justification of the rapid appreciation of science, and especially of that branch of science with which we are particularly concerned, in the public and administrative eye. The sudden incidence of new scientific modes of military and naval attack and the quick improvisation and development of equally scientific means of reply, both of which have been so frequently exhibited during the past five years, must have seemed uncanny to the lay observer, who only realised the effects but did not understand the causes.

At the present time, however, most Fellows of this Society have little leisure to reflect on the ghastly tragedy in which it has been our privilege to assist; the curtain has fallen upon this, but is rising again on the greatest epoch in the history of the world. The coming struggle for scientific and industrial position, on the results of which must rest the whole intellectual, artistic, and material future of our race, will call for longer, greater, more persistent and more intelligent effort than any which we have hitherto exerted. We are forced to consider whether we have reason to hope that the recent lessons have been well brought home and whether the free play given to scientific creation and production during the last five years is to persist unhampered in the future. For purposes of war our administrators gave every incentive to scientific investigation; money, men, and material were provided for the asking, free from Treasury control, free, in fact, from all control other than that of the scientific worker able and willing to organise and execute a necessary piece of work.

I see no reason to think that the lesson has been properly learnt and every reason to anticipate a re-establishment of that parsimonious treatment of scientific effort which seems now to belong to a past age, but with which we were all well acquainted five years ago. The control of scientific research is again leaving the hands of the scientific man and being resumed by the lay administrator. The old remark has been resuscitated quite recently that "it is a common-place among administrators to fear the expert." The non-technical administrator has no means of distinguishing the expert from the charlatan; he has perforce to regard the scientific expert as the lineal descendant of the "adept" of alchemical times whose claim to recollection is based upon the adroitness with which he was able to divert public funds to his own base purposes.

It is quite clear that if scientific research is to be assisted by the State—and unless so aided it will languish and carry with it into decadence every activity of the Empire—it must be adminis-

tered by men of scientific training and eminence; any other mode
of procedure will necessarily lead to the strangulation of scientific
effort by departmental red-tape.   In this connexion it is again
instructive to refer to American practise; our blood-relatives across
the Atlantic had three years in which to study in peace the efforts
which we were making in war, and it cannot but be useful to
observe the manner in which they propose to profit by our experi-
ence.

In 1916, President Wilson, a University professor and an expert,
now one of the most imposing figures in terrestrial affairs, called
upon the National Academy of Sciences at Washington to nomin-
ate the members of a " National Research Council "; the object of
this new organisation was stated to be that of co-ordinating the
scientific work of the country in order that the scientific problems
both of war and of peace might be more efficiently solved.   The
National Research Council is under the presidency of one of the
most eminent among the active American men of science, Professor
George E. Hale, of the Mount Wilson Observatory, and has large
funds at its command for research purposes.   Two points are con-
spicuous in connexion with the American programme : first, the
substitution of the professional lay administrator by the ordinary
office staff; secondly, the recognition of the close interdependence of
pure and applied science.   The contention which has long been
advanced in this country, that an adequate output of purely aca-
demic chemical research work and the existence of a flourishing,
fine chemical industry are mutually essential, is here tacitly ac-
cepted; the former seeks in the industries remunerative positions
for the products of its training, and the fine chemical industry looks
to the scientific investigator for inspiration and new directions for
enterprise.   The nation which possesses an extensive organic chemi-
cal industry controls chemical warfare, the production of pharma-
ceutical and photographic products, the textile industry, and many
other great departments of human activity.

The operations of the great American organisation for the stimu-
lation of scientific research work are already making themselves felt.
They have produced just recently an entirely novel method for
oxidising naphthalene to phthalic acid, presumably by the use of
atmospheric oxygen and a catalyst, which gives a 95 per cent. yield,
and are responsible for the huge nitrogen fixation scheme now under
installation in the States.   These two illustrations alone, the one
small and the other large, leave us in no doubt as to the influence
which the National Research Council is destined to exert on scien-
tific and technical progress throughout the world.

If British science is to make itself adequately felt in the great

intellectual and material advances of the near future, British men of science must be entrusted with the initiative power and the command of money which they have enjoyed during the past few years; unless this is done our Empire will, as before, continue to fall behind other great nations as a contributor to the increasing mass of pure and applied scientific knowledge.

In an address which I had the honour of delivering in this room a year ago attention was called to the necessity for closer co-operation between the large Societies representing the various chemical interests in Great Britain. During the past year action has been taken in this matter, and some fifteen of the Societies have collaborated in the establishment of a Federal Council for Pure and Applied Chemistry, the functions of which is to advance, safeguard, and voice the interests of chemical science. The Federal Council consists of representatives nominated by the component bodies, and is already occupying itself actively with the questions within its purview; it has moved with some success in connexion with the claims of experimental science to recognition in the recently established scheme for education within the Army, with the provision of fine chemicals for research purposes, with the remuneration of scientific posts, and with other matters. The Federal Council will continue to apply itself to those questions which are of importance to chemists as a class leaving more specific chemical interests to be dealt with by the appropriate constituent societies. A very similar project for the consolidation of the larger chemical interests is in course of execution by our French colleagues.

It is beyond question that a central house for accommodating the chemical societies in a manner more proportionate to their importance than is at present possible should be provided, that a common chemical library far more complete than any now available in this country should be at our service, and that some comprehensive scheme for the publication of compendia of chemical knowledge should be put into operation. A very imposing and costly programme confronts the recent amalgamation of chemical interests, but the universal approval which greeted the proposition for creating a Federal Council for Pure and Applied Chemistry is a happy augury for the future usefulness of the new organisation.

OBITUARY NOTICES.

JOHN PERCY BATEY.

BORN MARCH 22ND, 1889; KILLED IN ACTION APRIL 9TH, 1918.

JOHN PERCY BATEY, M.Sc.(Tech.), was educated at the Manchester Municipal Secondary School, where he was awarded a three years' scholarship to the Manchester School of Technology. He took the degree of B.Sc.(Tech.) in 1908 when nineteen years of age, and was also awarded the Schuster Research Scholarship. Twelve months later he was made M.Sc.(Tech.). For a time he was lecturer and demonstrator, and in 1911 he became assistant to Dr. Liebmann, of Weybridge, where he remained until he enlisted in January, 1915.

He joined the Public Schools Battalion, the Middlesex Regiment, transferring later to the Royal Engineers, and went to France in August, 1915. He was promoted to the rank of Company Sergt.-Major in September, 1916. In 1917 he was awarded the Belgian Croix de Guerre, and in 1918 the D.C.M.

With regard to the D.C.M. the *Gazette* published the following:

"He volunteered on no less than eleven times in one month to conduct parties carrying rations and supplies over a very much exposed area that was being heavily shelled by the enemy to gun emplacements in the front line. The fine example of courage and devotion to duty of this warrant officer had an excellent effect on the N.C.O.'s and men of his company."

F. B.

LIEUT. CHARLES WILLIAM DICK.

BORN APRIL 10TH, 1895; DIED ON SERVICE NOVEMBER 9TH, 1918.

LIEUT. CHARLES WILLIAM DICK, R.A.F., died of pneumonia on November 9th last in Cliff Military Hospital, Felixstowe. Mr. Dick, who was the younger son of the late Mr. J. Dick, schoolmaster, North Shields, took 1st Class Honours in his Inter B.Sc.(London) on leaving Rutherford College, Newcastle-on-Tyne, in June, 1912,

and in the autumn of the same year gained an open science scholarship at Cambridge University and became a scholar of Trinity Hall in the autumn of 1913. He passed his final for the B.Sc.(Lond.) in 1914, and on completing two years' residence he postponed further study to become a chemist at Messrs. Curtiss' and Harvey's explosives works at Cliffe, near Chatham, and whilst there was elected a Fellow in 1917. He joined the Meteorological Section of the R.N.V.R. in April, 1918, and after completing his training was appointed meteorological officer at Felixstowe Air Station, and on the creation of the R.A.F. was transferred to its establishment in August, 1918.

J. E. D.

JAMES HECTOR BARNES, D.Sc.

BORN 1879; DIED 1917.

" I AM sorry to say I have been in very poor health all the summer and had to take six weeks' leave in Kashmir this autumn ; it was no holiday, however, for I spent four weeks of it in bed with an irregular pulse—the old story of India, malaria, and, the doctors say, overwork. I hope to come home next summer, for I do not think I can stand another Indian summer here without first having a rest in a decent climate. I shall look you up then, and I hope you will be kind and put me in the way of being useful while at home on leave as I really cannot idle about."

These extracts are from a letter dated November 30th, 1916, received from Hector Barnes. He did not come home, and his prophecy was fulfilled; he did not stand another Indian summer, but at the age of thirty-eight, in the fullness of his intellectual powers, with high hopes and with great opportunities opening before him, he died in India. It is difficult indeed to write any adequate record of the worth and work of such a man. The scientific work which he accomplished, had it been carried out in the most favourable environment, was such as any chemist might be proud to have to his name. But it was carried out under conditions which would only be met by a man of heroic temperament. Such a man Barnes in truth was.

In the plains of Northern India, at Lyallpur, a remote station, on land recently transformed from a sterile desert into a luxuriant agricultural colony by the marvellous system of Indian irrigation, Barnes betook himself in 1906. Born in 1879, he had received his scientific training at the University of Birmingham, where he

studied chemistry and physics under Professors Frankland and Poynting and graduated B.Sc. He had previously been apprenticed to Messrs. Southall and Barclay, pharmaceutical chemists, and the experience of the practical conditions of manufacturing operations which he there acquired no doubt added greatly to his equipment for the work that was in store for him. At Lyallpur he held the position of agricultural chemist to the Punjab Government and professor of chemistry in the Agricultural College, then at the stage of inception. He threw himself wholeheartedly into the work of designing the chemical laboratories, and in 1908 his responsibilities were increased by his appointment as Principal of the College. A year later the College was open for the reception of students. There was an immediate response, as there is to every new educational enterprise in India; but when it was found that the College was not, as it was expected to be, a certain path to Government service, the numbers fell with great rapidity and any belief that there was widespread zeal among neighbouring landowners for agricultural science could not be sustained. Barnes, however, had cherished no illusions, and he knew from the first that the foundation on which he must build was sound scientific research addressed as directly as possible to vital questions of Indian agriculture, and to this he and his colleagues bent their energies. It is not easy to give an idea of what that meant. The physical obstacles imposed by the climate and ever-recurrent sickness, the isolation from the scientific world and from the meagre supplies of apparatus anywhere available in India—these alone might daunt a strong man. Add thereto, only in a more intense form, what we have in England—Government officials in authority whose "humanisation" has precluded the slightest knowledge of what science is, what it does, and how it can be applied to do more—and it may be understood that it is only the very exceptional man who can succeed. This Barnes did in the most conspicuous degree. Standing in the laboratories at Lyallpur after some hours' journey from Lahore through great tracts of solitude and finding apparently all the resources of a European university science department and men busily engaged in employing the experimental methods of modern physical chemistry in the elucidation of fundamental problems in agriculture, the greatness of the achievement was very striking to the imagination. Within a stone's throw were the mud walls of an Indian village with its population living unchanged in the beliefs, the thoughts, the habits of life and work that belong to distant centuries of the past.

The chief lines of work on which Barnes was engaged were salt lands and their reclamation; seepage and the rising of ground water-

level under irrigation conditions; the sugar cane and the sugar industry in the Punjab; the intensity of solar radiation; the Kangra tea industry; the chemical aspect of weevil attacks upon wheat. It is to be feared that his published papers and records will give no adequate idea of the comprehensive plans which he had in his mind in relation to the elucidation of these problems. He talked of them eagerly and in the most interesting way, showing at once his sound knowledge of fundamental science and his appreciation of practical conditions. He had erected a workshop and turned out from it many of the fine tools required in his work, and his laboratory methods exhibited the play of great experimental skill and resource. Space does not admit of any extended account of these investigations, but a little more may be said of one of them. On his last visit to Lyallpur in 1914 the writer was taken by Barnes to Narwala. This spot is twelve miles distant from Lyallpur, and is, or was, infertile salt-land, that is, land which owing to triumph of evaporation over rainfall has become impregnated with a variety of salts, carbonates, chlorides, and sulphates, especially of sodium, calcium, and magnesium, evident as a crust of " white alkali " or " black alkali " upon the soil. This condition of soil has been the subject of much study in America, but Barnes believed that the work had " failed to prove useful and practical for want of a better knowledge of the scientific principles of the causes of sterility. If such causes had been first investigated time and money would have been saved, and in the end the *practical* result would, as it always does, justify the scientist." Accordingly, Barnes set himself to study as closely as possible the physical, chemical, and biological aspects of the problem. Having satisfied himself of the principles involved, he applied himself to the practical problem of redeeming the land at Narwala, and at the time of the visit referred to a tract of infertile land was being mole drilled. Leaving fields where the leisurely ryot was urging his bullock to pull the wooden plough and gently scratch the surface soil, one passed to the Narwala tract where a Yorkshire artisan was found in contest, doubly bitter to him by the futility of his native tongue, with native inaptitude in dealing with a steam-driven mechanical monster from Leeds. The plan was to mole drain the land and then irrigate out so much of the salts as was shown by Barnes's biological methods to be necessary. The results of this trial were extraordinarily successful, and it is scarcely possible to believe that the luxuriant crops (of which photographs afterwards arrived) can have been grown on what was just before the war a stricken desert. Barnes in the end estimated that the system of reclamation would pay between 300 and 400 per cent. on the capital outlay, and its general application would, of course, add

millions to the wealth of India. He was proposing also to apply the system to non-irrigated areas by the use of water pumped from the subsoil.

In 1914 Barnes married Nora, daughter of the late Colonel Francis Thomas Steven, Indian Army.

As soon as the war began he bestirred himself to bring into action all the scientific and material resources that India could supply, but it is impossible at present to quote his important observations on this subject.

Shortly before his death Barnes, not without some reluctance on his part, left Lyallpur to take up at Pusa the post of chief agricultural chemist to the Government of India. What he might have accomplished from there it is idle to conjecture, but the thought of it only deepens the sense of calamity both to India and to Science that surrounds his untimely death.

Barnes was every inch a man and an Englishman. When the writer first saw him he had just come from among his students in the playing fields and was in football attire, a splendid figure of a man, eager, resolute, honest, and kindly. He was beloved by his students and colleagues and respected by everyone. In summing up his qualities in our mind it is impossible not to be struck with the strength and number of endowments that are needed to produce the type of man who is to be the true pioneer of progress in India— endowment of body, mind, and spirit. Happily, such pioneers have been found in the past. They will long be needed in the future of India, and it is difficult to think of any better service to mankind than is open there to those who can bring themselves to the standards that ruled the life and work of Hector Barnes. At Lyallpur his portrait and an annual prize have been set up to preserve his memory, and shortly before his death he was made a Doctor of Science of his University of Birmingham. His work and influence will endure in many fields and many hearts.

A. S.

GEORGE CAREY FOSTER.

BORN 1835; DIED FEBRUARY 9TH, 1919.

IN the death of Professor Carey Foster in his eighty-fourth year on February 9th, there are many who will feel the loss of a kind and generous friend, to whose gentle sympathy and encouragement much of the happiness, as well as much of the success, of their own lives has been due. A man of extreme modesty and of high

if not commanding ability, Carey Foster had made few direct contributions to scientific literature; but the soundness of his judgment, his almost passionate love of exact knowledge, and his enthusiasm, earned the respect of all, and made his presence invaluable on the many committees of learned societies, the British Association, and the various university boards of which he became a member. An extreme diffidence and a nervous shyness that was not without a peculiar charm to those who came to know him well, as well as a hesitation to express a definite opinion on subjects on which he did not feel on the firmest ground, made it easy to undervalue the services he rendered to science and education during the course of a long and active life.

George Carey Foster was the only son of George Foster, a calico printer and a Justice of the Peace for Lancashire and the West Riding of Yorkshire, and was born at Sabden, in Lancashire, in 1835. After an early education at private schools, he entered as a student at University College, London, where his studies were at first mainly directed to chemistry. He graduated in Honours and with a prize in chemistry in his twentieth year, and acted for some years as chemical assistant to Professor Alexander Williamson, who had then occupied the Chair of Chemistry for six years, and a warm attachment and regard sprang up between the two men. He left England in 1858, and spent some years in study at the foreign Universities of Ghent, where he was a student under Auguste Kekulé, at Paris, and at Heidelberg.

At this time, however, while he continued his chemical studies, his interest became more and more directed to physical science, which was then assuming a position of increasing importance through the work of such men as Clausius, Lord Kelvin, and Clerk Maxwell, and it was natural that the refined accuracy of physical measurements and the readiness which they admitted of mathematical treatment should have presented a strong attraction to a man of his type of mind. The first evidence of his new interest was the appearance in 1863 of two articles on "Heat" in the first edition of Watts's "Dictionary of Chemistry." These articles, extending together to more than 150 pages of closely printed matter, formed an admirably concise and critical statement of the position of an important branch of science, and at once established Carey Foster's reputation as a clear thinker and able exponent of physics.

In the meantime, in 1862, Carey Foster had accepted an invitation to assume the duties of professor of natural philosophy at the Andersonian University, Glasgow, and in 1865 he was encouraged by his friend and former teacher, Williamson, to

become a candidate for the vacant professorship of experimental physics at University College. His election was mainly due to the high reputation he had established as the author of the articles in Watts's Dictionary, and in October, 1865, he entered on his career at the London College, of which he was elected a fellow in 1867, and with which his name will always be associated. He resigned his professorship in 1898, at the age of sixty-three, but was recalled to act as principal of the college for a period of four years from 1900, during a critical time in its history. The last years of his life were spent in the quiet and refinement of a country life on a small estate at Rickmansworth, although, until quite near the end, he was always ready to place his services at the disposal of the educational causes that had been so near his heart in former times. He became a Justice of the Peace for Hertfordshire, and took an interest in politics, in which he was a supporter of the Liberal Party. Towards the end of 1917, after the death of his wife, he began to feel the weight of advancing years, but up to within two weeks of his death he was at work on manuscripts submitted to him for publication in the *Philosophical Magazine*. At the end of January of the present year he had a slight attack of congestion of the lungs, which his heart was not strong enough to resist, and, after gradually becoming weaker, he passed away in the presence of his children on February 9th.

Carey Foster's contributions to chemistry were published between 1857 and 1867. The writer, who is profoundly ignorant in chemical matters, is indebted to his friend, Dr. Forster Morley, for the following summary of these researches. Dr. Morley was engaged in several physical researches under the direction of Carey Foster while a student at University College, and was intimately acquainted with him during the remainder of his life.

"The first paper by Carey Foster appeared in the notes and abstracts appended to the British Association Reports for 1857. It is entitled 'On suggestions towards a more systematic nomenclature for organic bodies.' Gerhardt having introduced the term *homologous* to denote that two carbon compounds differed in their formulæ by CH_2 or a multiple thereof, Foster now proposed a new adjective, *isologous*, to indicate a difference of H_2 or a multiple of H_2. This adjective is still employed to denote the difference. He further suggested words composed of two Greek numerals, the first of which related to homology and the second to isology. Thus *deutritic* would mean 'belonging to the second homologous series and the third isologous series.' This suggestion, together with many other ingenious proposals for new nomenclature, did not receive support from other writers

"In 1859 Carey Foster presented a preliminary report to the British Association 'On the Recent Progress and Present State of Organic Chemistry' (*Rep. Brit. Assoc.*, 1859, 1). This was a review of recent work, particularly from the point of view of the development of ideas about formulæ.

"In the Chemical Society's Quarterly Journal (1860, **13**, 235) we find a paper 'On Acetoxybenzamic, an Isomer of Hippuric, Acid,' by G. C. Foster. It is dated Ghent, 1860, and is an account of a very careful piece of work carried out under the direction of Professor Kekulé, and describes the first preparation of *m*-acetylamino-benzoic acid, which is shown to be related to hippuric acid, from which it might, in imagination, be derived by an interchange between the radicles of benzoic and acetic acids.

"A paper published in 1861 'On Piperic and Hydropiperic Acids' appeared in the Chemical Society's *Journal* (1862, **15**, 17; also in *Rep. Brit. Assoc.*, 1861, 78, and *Annalen*, 1862, **124**, 115). In this it is shown that piperic acid, $C_{12}H_{10}O_4$, is reduced to hydropiperic acid, $C_{12}H_{12}O_4$, and a large number of the salts of the latter are described.

"The most important chemical work carried out by Carey Foster is contained in three papers published in conjunction with Matthiessen. The first is entitled 'Preliminary Notice of Researches into the Chemical Constitution of Narcotine,' and was read before the Royal Society in 1860 (*Proc. Roy. Soc.*, 1861, ii, 55; *Phil. Mag.*, 1861, [iv], **22**, 398). In this the authors establish the formula $C_{22}H_{23}O_7N$ for narcotine, and show that this alkaloid gives off methyl iodide when heated with hydriodic acid. The oxidation of narcotine to opianic acid is discussed, and the formula for opianic acid, $C_{10}H_{10}O_5$, correctly determined. It is also shown that, on heating with concentrated potash, opianic acid can be neatly split up into meconin and hemipic acid. A new acid, cotarnic acid, was obtained by the gentle oxidation of cotarnine.

"The second paper on this subject, entitled 'Researches into the Chemical Constitution of Narcotine and of its Products of Decomposition,' was published in 1863 (*Phil. Trans.*, 1863, 345; an abridgment is given in *J. Chem. Soc.*, 1863, **16**, 342). The authors here describe how, by acting on hemipic acid with hydriodic acid, an acid, $C_7H_6O_4$, which they call 'hypogallic acid,' but which is now known as protocatechuic acid, is obtained. As an intermediate product they isolated 'methylhypogallic acid,' now called '*iso*valeric acid.'

"The third paper is entitled 'Researches into the Chemical Constitution of Narcotine and its Products of Decomposition, Part II,' and was read before the Royal Society in 1867 (*Proc. Roy.*

Soc., **16**, 39; *J. Chem. Soc.*, 1868, **21**, 357). It is shown that opianic acid, when heated with hydrochloric or hydriodic acid, forms methyl chloride or iodide, and a new acid, 'methylnoropianic acid,' $C_9H_8O_5$. Thus, opianic acid may be called dimethyl-noropianic acid. Methylnoropianic acid yields with nitric acid nitromethylnoropianic acid. Meconin, on heating to 100° with concentrated hydrochloric or hydriodic acid, yields methyl chloride or iodide and methylnormeconic acid, or, rather, methyl-normeconin, $C_9H_8O_4$. By similar means, narcotine can be converted into methylnornarcotine, $C_{20}H_{19}O_7N$.

"These three papers by Foster and Matthiessen made a long step forward in the knowledge of the constitution of the alkaloids, and may, indeed, be termed classical. The accuracy of the work has been amply confirmed by subsequent investigation.

"While this work was in progress, Carey Foster published two papers, entitled 'On Chemical Nomenclature, and chiefly on the Use of the Word *Acid*.' Both appeared in 1865 (*Phil. Mag.*, [iv], **29**, 262; **30**, 57). In these he protests against the word *acid* being used to denote an oxide, and recommends that SO_2 be called sulphurous oxide, SO_3 sulphuric oxide, and $C_4H_6O_3$ acetic oxide.

"In 1869 Carey Foster took part in a discussion on the atomic theory, held at the Chemical Society, the subject having been introduced in a lecture by Professor A. W. Williamson. An account of the discussion will be found in the Chemical Society's *Journal* for 1869.

"Carey Foster's work in chemistry shows that if he had decided to devote himself to that science he would have taken a distinguished position among his colleagues. He was a member of the Council of the Chemical Society from 1865 to 1868, again from 1872 to 1875, and again from 1885 to 1886, and Viice-President from 1888 to 1890. His Fellowship of the Society dates from 1856."

During the early years at University College, Carey Foster made a number of contributions of minor interest to scientific journals, but his first important paper, "On a Modified Form of Wheatstone's Bridge, and Methods of measuring Small Resistances," was read before a meeting of the Society of Telegraph Engineers in 1872 (*Telegraph Engineers' Journal*, 1872—1873, **1**, 196). Previous to this date, Wheatstone's bridge had provided electricians with a convenient and fairly accurate method for comparing resistances, and, as is well known, the result of the experiment expresses the ratio of one resistance to the other. Carey Foster,

however, so modified the bridge method that the difference between instead of the ratio of the resistances was determined. The advantage of the change is only apparent where the resistances to be compared are of nearly equal value, as is generally the case, for instance, in the testing of standard coils; but where this condition is fulfilled, the new method transformed the bridge method from being merely a fairly accurate means of measurement into one of the most refined accuracy, comparable with that attained in the use of a sensitive balance. It also supplied the means of dealing with a very small resistance, such as that of a short, thick wire, by determining the difference between it and the zero resistance of a short copper bar, and it was, indeed, for this alone that the method was first suggested. Carey Foster's method has proved of the highest value to the science of exact electrical measurement, and has made it possible to issue standards of electrical resistance of an accuracy that would otherwise have been impossible of attainment. Alike in its simplicity and its refined accuracy, the method is thoroughly characteristic of his mind. He further showed how the principle involved might be applied to the important process of calibrating the wire of the bridge.

In 1881 Carey Foster published "An Account of Preliminary Experiments for the Determination of the Electromagnetic Unit of Resistance, in Absolute Measure" (*Rep. Brit. Assoc.*, 1881, 426). The accurate determination of this important unit had been undertaken by the British Association in 1863, and the value that had been accepted in this country, as well as widely in other parts of the world, was expressed in the "B.A. unit of resistance," the value of which had been determined by a Committee of the Association consisting of Clerk Maxwell, Fleeming Jenkin, and Balfour Stewart. The classical method of experiment adopted by the Committee consisted in revolving a large, flat, closed coil of insulated copper wire about a vertical diameter in the earth's magnetic field and measuring the consequent deflexion of a magnet suspended at its centre. The deflexion was due to the induced current developed in the coil, and this depended on its resistance as well as on the intensity of the earth's magnetic field. The last, however, affecting the induced current and the deflexion equally, although in opposite senses, disappeared in the final equation that expressed the result of the experiment, leaving a relation between the resistance of the coil, its geometrical form and dimensions, and the speed of its revolution.

During the years that had elapsed since the issue of the B.A. unit, the results of other measurements had led to a growing conviction that it was appreciably too small, and Carey Foster

described an experiment in which, whilst the general principle of
the British Association experiment was maintained, it was modified
in an important detail. The two ends of the wire composing the
coil were unconnected throughout the greater part of its revolu-
tion; but for a short interval, the centre of which coincided with
the transit of the plane of the coil through the magnetic meridian,
they were placed in connexion through sliding contacts with the
two ends of a standard resistance coil that formed part of an
"auxiliary" circuit in which a steady current was maintained by
a thermopile. By the principle, originally applied by Poggen-
dorff in the potentiometer, no current is developed in the coil if
the electromotive force developed in it by its rotation in the earth's
magnetic field is equal to the fall of potential between the two
points in the auxiliary circuit with which it is connected, this
being the product of the current supplied by the thermopile and
the resistance of the standard coil, and the method of experiment
consisted in so regulating the current of the thermopile that the
deflexion of a sensitive galvanometer included between the
revolving coil and one of its points of connexion with the auxiliary
circuit should disappear, whilst at the same time the deflexion of
the magnet of a tangent galvanometer included in the auxiliary
circuit was recorded. The general principle is simple, and a rela-
tion is readily established between the resistance of the standard
coil, the deflexion of the magnet of the tangent galvanometer, the
geometrical form and dimensions of the revolving coil, and its
speed of revolution.

The chief refinement that Carey Foster hoped to effect in this
modification of the original experiment consisted in the possibility
of the *direct* determination of the resistance of the standard coil.
In the original experiment, the resistance determined was that of
the revolving coil, and the resistance of the standard could only
be obtained by subsequent comparison. To obtain the maximum
induced current, it was essential that the revolving coil should be
wound with copper wire, and as the resistance of copper with that
of all pure metals is seriously affected by changes of temperature,
it was necessary that the temperature of the coil should be known
with great accuracy during the time that the experiment was in
progress, a very delicate matter. In Carey Foster's method, how-
ever, the resistance of the standard coil was directly determined
while it formed a part of a fixed and independent circuit. The
wire composing it might equally well be of copper or of one of
the many alloys the resistances of which are scarcely affected by
changes of temperature, whilst it was an easy matter to determine
its temperature with great accuracy. Further, the new method

reduced the correction for the self-induction of the revolving coil, an important and rather delicate detail in the original experiment, to insignificant proportions, but, at the same time, it unfortunately introduced the necessity of taking its capacity into consideration, a feature that Carey Foster did not probably at first realise.

The apparatus for carrying out the experiment was constructed with great refinement, and was erected at University College, and a series of preliminary experiments were made by Carey Foster with the assistance of Mr. G. W. von Tunzelmann. These experiments showed that the method was capable of yielding consistent results, and there is no doubt that a far higher consistency would be possible if they were repeated in a modern laboratory more completely removed from the disturbing magnetic influences of large masses of iron of continually varying temperature. The results were not, however, sufficiently consistent to satisfy the critical judgment of Carey Foster, and the experiment was abandoned. Whilst they were in progress, Lord Rayleigh and Professor Schuster were engaged in repeating the original experiment, adopting precautions that experience of the intervening years had been shown to be necessary, and in 1882 they published an account of their experiments, and during the next ten years independent evidence supplied by other methods has shown the value they obtained to be a close approximation to the truth.

In 1886 Carey Foster contributed a paper to the Physical Society of London "On a Method of determining Coefficients of Mutual Induction" (*Phil. Mag.*, 1887, [v], **23**, 121—129), the method depending on the comparison between the coefficient of mutual induction of two coils and the capacity of a condenser. On forming or breaking a current in one of two coils, the primary, a discharge of electricity takes place through a neighbouring, secondary, coil, the discharge being determined by the coefficient of mutual induction of the two coils; also, if the coatings of a condenser are connected to two points of the primary circuit, a charge, proportional to the resistance of that part of the circuit that is included between the two points of connexion, enters the condenser, and will be discharged on the cessation of the primary current. To combine these two examples of "ballistic" discharge, Carey Foster succeeded in so connecting the two circuits that, on the break of the primary current, the condenser was discharged through the secondary circuit in the opposite direction to that of the induced discharge, and on varying the charge of the condenser by regulating the resistance between the points of its connexion with the primary circuit, its discharge and that of the induced current neutralised one another.

The disappearance of discharge in the secondary was indicated by a galvanometer, and a simple relation was given between the coefficient of mutual induction of the coils and the capacity of the condenser. The capability of the method had been thoroughly tested at University College by Mr. F. Womack, and it had been shown to be capable of yielding results of a high order of accuracy. Carey Foster's method of determining the coefficient of mutual induction between two circuits has taken its place among the accurate methods of electrical measurement.

In 1876 Carey Foster devised a method, based on the principle of Wheatstone's bridge, of tracing the equipotential curves in a sheet of tinfoil conveying an electric current, and in collaboration with Sir Oliver Lodge he published two papers, "On the Flow of Electricity in a Plane Conducting Surface" (*Proc. Phys. Soc. London*, 1876, **1**, 113, 193), in which this method of experiment was adopted. A further paper by Carey Foster and the present writer, "On the Difference of Potential required to give Sparks in Air," was presented to the Physical Society in 1884 (*Chem. News*, 1884, 114). In the method of experiment adopted in this research, potential differences were measured by a modified form of absolute electrometer that had been designed by Carey Foster and that was found to supply an accurate method for measuring potential differences necessary to produce sparks of from 0·1 to 5 cm. in length.

Among Carey Foster's other publications were further articles on "Heat," "Thermodynamics," "Electricity," and "Magnetism" in later editions of Watts's "Dictionary of Chemistry," and in these he fully maintained his reputation for accuracy, clear judgment, and power of scientific exposition. In later years he published a text-book on electricity in collaboration with Professor A. W. Porter.

Carey Foster became a member of the British Association in 1857, and continued to take an active part in its proceedings until late in life. Besides his direct contributions, to which reference has already been made, he was a member of a number of its committees, the more important of which were those on "Standards of Electrical Resistance," "The Selection and Nomenclature of Dynamical and Electrical Units," "The State of Knowledge of Spectrum Analysis," and "Electrolysis." As President of the Mathematical and Physical Section in 1877, he gave an address on "The Mutual Relation between Mathematics and Physics," in which he dwelt on his favourite theme of the importance of accurate measurement as the foundation of discovery in science. He was Treasurer to the Association from 1888 to 1904. He was one of

the founders of the Physical Society of London, the first meeting of which was held in 1873, and of which he was President for two years from 1887. He acted as President of the Society of Telegraph Engineers, now the Institute of Electrical Engineers, in 1880 and in 1881. He was elected to the Fellowship of the Royal Society in 1859, acting as one of its Vice-Presidents from 1891 to 1893, as well as from 1901 to 1903, and he took a keen interest in the work of Kew Observatory Committee of the Society. He received the honorary degrees of LL.D. from Glasgow and D.Sc. from Manchester.

From the first, Carey Foster took a deep interest in the reconstitution of the University of London. Whilst fully recognising its services to education in its earlier days, he was sensible of the grievous anachronism by which the University of the greatest city of the world should continue to be solely engaged in examining and in conferring degrees. He had a high ideal of a university as a body of men and women earnestly engaged in the pursuit and extension of knowledge rather than in preparation for examinations, and he strove without ceasing to bring about the foundation of a university in London that should be worthy of it. He was an active member of the many early committees the aims of which were a constructive policy that should achieve his ideal, and he felt keen disappointment when the conflicting of many interests made it impossible of full attainment in the present university, although it received his full and loyal support. He never ceased, however, to look forward to a time when, by further reconstruction, London should possess a university fully worthy of its position, and he welcomed Lord Haldane's Report as indicating the possibility of a further step in this direction, and possibly its full attainment.

The writer is indebted to Sir T. Gregory Foster, Provost of University College, for a sketch of Carey Foster's work while acting as Principal of the College from 1900 to 1904.

" Dr. G. Carey Foster resigned the Quain Chair of Physics in 1898. It was a time of crisis in university affairs in London, as the reconstitution of the University was pending.

" In view of the impending reconstitution, the Council of University College appointed a special committee to consider the position of the College. On the recommendation of this committee, the office of Principal, later changed to Provost, of the College was instituted. Dr. Carey Foster was invited to be the first occupant of this office. He held it from 1900 to 1904.

" In his capacity of Principal, he was appointed to represent University College on the Senate of the University under its new

constitution. He threw himself heartily into the new problems that arose, and brought to them all his ripe judgment and experience.

"It soon became evident that the new constitution, under which the University was given a teaching side as well as an examining side, made it desirable that University College, which had been originally founded to be the University of London, should be merged into the reconstituted University. Dr. Carey Foster took an active share in the negotiations that led up to the incorporation of the College in the University. He regarded it as 'a step towards securing unity of aim and interest in all that relates to advanced education and the promotion of original research in London.' He hoped that it was the beginning of a movement that would lead to the concentration and the consolidation of university work in London.

"This view is expressed in the final paragraph of his sketch of the History of University College, which is as follows :

"'The step taken by University College has been followed by King's College, which was incorporated in the University on September 1st, 1909. It may be hoped that similar action will be taken by other analogous bodies, and that in course of time the University of London, perhaps with some modification of its present constitution, may become a centre about which the various bodies in London that are qualified to take part in university work may be united into a single organised system, in which they shall supplement instead of competing with each other, each doing the work for which, by its special circumstances, it may be best fitted.'

"During the four years of his Principalship, great progress was made in various directions in the reorganisation and development of university work in London. The plans for the removal of University College School were matured. The buildings formerly occupied by the School were, as a consequence, set free for university purposes. The accommodation provided at University College for university work was materially increased. There was a rapid growth in the intellectual and social activities of the College, and in these Dr. and Mrs. Carey Foster took a prominent share."

At an early period of his work at University College, Carey Foster recognised the importance of practical work in physics as an essential element in scientific education. The first physical laboratory for students had been opened by Magnus at Heidelberg in 1846, and it was followed in 1863 by the addition of a physical laboratory to the University of Berlin. From 1845, Lord Kelvin

had invited his senior students to work in his laboratory, for a time a disused wine cellar, at Glasgow, and his example was followed by Carey Foster, who thus introduced the teaching of practical physics in this country. At the beginning, this work formed no recognised part of the College curriculum, but regular practical courses in physics were arranged in 1867, the laboratories at that time consisting of two of the College rooms, only one of which was fitted with benches. Later, a third room in the basement, known as the "dungeon"—it was indeed a veritable dungeon—was added, and the privilege of working in it was reserved for the professor and students engaged in research. For some years, the only apparatus available was of the simplest character, but instruments were being constantly designed by Carey Foster himself, whilst the designs were executed by a clever Scotch mechanic, William Grant, who acted as his assistant during the whole time of his professorship, and without whom no reference to the laboratory would be complete. Grant, who was quite a character in his own dour way, became a permanent feature of the Physical Department. His love of the apparatus, so much of which he had constructed, and the agony he experienced in seeing it misused, made him a source of terror to all students other than those few who proved themselves worthy to be entrusted with it; whilst many will remember with humiliation his lofty refusal of the tip that was occasionally offered, either from gratitude or from a desire to acquire merit. He was of the most faithful of servants, and was devoted to Carey Foster, whilst each regarded the other with a simple affection of which both alike were worthy. Sir Oliver Lodge, who was a student in the laboratory in those days, and who later became Assistant Professor of Physics at the College, has rendered a grateful as well as a graceful tribute to the educational value of the work done in the old physical laboratory of University College (Letter to *Nature*, December 3rd, 1908).

In the years that followed, physical laboratories for students were opened at other colleges, and it was inevitable that, as many of these were attached to new institutions in which it had been possible to design the buildings with a view to their subsequent use as laboratories, the simple equipment at University College should have been left behind. Carey Foster, in consequence, continually urged the governing body of the College to undertake the building of a physical laboratory that should be worthy of its traditions, although, no doubt by reason of financial considerations, his representations were for a long time without success. At length, however, he had the satisfaction of preparing the plans for the present laboratories, which were opened to students in

1893, and form a fitting memorial to the value of his work as Professor of Physics. There was an old asphalted tennis court within the College walls from which some of us have often returned in exhilaration, although with begrimed hands and flannels, and now only lives in memory; the building that now occupies its former site is the " Carey Foster" Laboratory.

His nervous manner prevented Carey Foster from ever becoming a good lecturer, and his failure in this respect was perhaps due, in addition, to a conscientiousness that made it difficult for him to be content with a simple statement that he knew to be only an approximate expression of a truth, and at the same time made him reluctant to adopt the customary method of illustrating physical laws by the use of simple, although entirely imaginary, experimental data. In place of these, his illustrations would often consist of the actual results of laboratory measurements, and the younger students, unless they were of a rather exceptional type, were apt to lose both attention and interest in the details of laborious computation. The more able students, however, were inspired by this very quality in their teacher. They grew to reverence exact expression and to regard it as the foundation of all scientific knowledge. They continually brought their difficulties to the Professor, and were encouraged to do so by his unlimited patience in dealing with them. It was not unusual to find Carey Foster surrounded by a small group of students engaged in close discussion half an hour after the close of a lecture, although the dining-room had long since claimed the attention of the rest of the College.

The same quality of enthusiasm for his work and his infinite patience in dealing with its smallest details appeared in his work in the students' laboratory. He never found lecturing easy, but after having given a lecture in the morning and having a further lecture for senior students in prospect at the close of a long afternoon, he would frequently come to the help of some duffer in difficulties in the laboratory, and would devote the best part of an hour to the details of a simple experiment in physical measurement. On these occasions, indeed, there was a danger of his being led by his own love of accurate detail, not only to conduct the whole experiment himself, making all the observations, but to carry out whatever computation might be involved, while the student looked on wonderingly, as from a distance. It may be that some who have worked in the old laboratory at University College in those days have preserved the scraps of paper covered with logarithmic calculations that Carey Foster often left on the

benches, all executed in his wonderfully neat writing, as a memento of the most patient of teachers and most lovable of men, but such prescience is rarely bestowed on youth.

His nervousness made conversation with Carey Foster difficult, even to those who came to know him intimately. Whilst, however, it remained a source of some embarrassment to them, his friends came to regard it as so essentially a part of him that it too became lovable, and they would have felt still more embarrassed if he had suddenly succeeded in overcoming it. Closely associated with his manner was a quaint and entirely original sense of pure humour, that found frequent opportunity for expression both in his professional work and in his private life. That his nervousness and hesitation did not arise from any defect in character would be shown, were any such evidence necessary, from his letters. In these, Carey Foster found no difficulty in expressing himself with perfect clearness and precision, whilst both were emphasised by the beauty and strength of his handwriting. It was in his letters, perhaps, that his quaint humour found its best opportunity for expression. Through the kindness of Mrs. Minchin, the writer has before him a number of letters written by Carey Foster to her husband, the late Professor G. M. Minchin, which are so characteristic that little apology is necessary for the introduction of a few short extracts. A close friendship existed between Carey Foster and Minchin, and in their unassuming simplicity and gentleness there was much resemblance between the characters of the two men. Carey Foster had a profound respect for Minchin's mathematical powers, and consulted him when he felt a doubt as to his own grasp of the mathematical treatment of a physical problem, whilst Minchin had an equally deep regard for Carey Foster as an authority on physical matters, and has expressed his regret to the writer that Foster's nervous manner, together with his extreme modesty, should have made it difficult for some, even of his friends, to realise his true greatness.

The first extract is from a letter dated 1882:

" My dear Minchin,

" The lesson of the day touching electric endosmose is written in the First Book of Wiedemann, beginning at the 392nd verse of the second chapter . . . wherein it is written how the ions do wander when a current passeth through their midst. This, I take it, is the whole secret of electric endosmose; the porous diaphragm causeth not the flow, but maketh the same manifest by hindering the return thereof."

The second is also dated 1882 :

" My dear Minchin,

"I hope the enclosed may serve your riverence's purpose. Sure, and it's bad I did not write before. But I had to think, and that goes slow.

" As to your telegraphic friend; let him take to himself a tangent galvanometer and a set of resistance coils, and sundry cells according to Daniell and Grove. . . ."

and then follow instructions as to what the telegraphic friend should achieve.

An extract from a letter referring to a fairly well-known man :

"The gentleman's surface integral suggests to me a considerable amount of self-esteem. But I am willing to believe that the charge is purely superficial. . . . I am told by a friend who knows him much better than I do that he is a good fellow."

And the last is from a letter written in 1887 congratulating Minchin on his marriage:

" My dear G. M. M.,

" I heard awhile ago that you had entered into combination and were no longer a dissociated atom. Accept my warmest congratulations and my fervent hope that you may appreciate the blessings of home rule more fully from year to year."

Several of the letters deal with Minchin's work with photo-electric cells.

The private life of Carey Foster was one of quiet beauty. His transparent honesty and high regard for truth earned him the respect of his friends, whilst has unvarying kindness and courtesy won their affection. In 1868 he married Mary Anne Frances, daughter of Andrew Muir, of Greenock. Recalling that time, Dr. Forster Morley writes :

"It seems only yesterday when my father (the late Professor Henry Morley) said to me, 'I have been walking round the Square with Carey Foster, who has just told me that he is engaged to be married, and has been speaking most charmingly on the subject of love of a man for a woman.'"

There was a striking resemblance between the character of Mrs. Foster and that of her husband, and she even acquired a suspicion of the nervousness that was so strongly marked in him, that, however, only accentuated a natural charm of manner in her.   There were born to them four sons and four daughters, all of whom are still living.   The mutual confidence that existed between Carey Foster and his wife, and the evident affection with which both parents were regarded by their children, gave a peculiar charm to the visits of the many friends who were always welcome to their home.   Mrs. Foster died in 1917, and a year and a-half later Carey Foster's body was laid to its last rest beside hers in the peaceful cemetery at Rickmansworth.

Among the number of Carey Foster's old students at University College who have become distinguished were Prof. W. E. Ayrton, Sir Oliver Lodge, Dr. H. Forster Morley, Prof. Viramu Jones, Prof. A. P. Chattock, Prof. J. A. Fleming, Prof. T. Hudson Beare, Prof. A. W. Porter, Prof. F. Womack, Prof. J. Sakurai, Sir Victor Horsley, and Prof. W. D. Halliburton.   It is from his having been first a student, then a demonstrator, and thereafter a friend of Carey Foster that the writer has been able to pay in this notice his last tribute to the memory of one he loved and admired.   A. H. FISON.

WILLIAM JOEL KEMP

BORN 1841; DIED MARCH 22ND, 1918.

WILLIAM JOEL KEMP was born at Bow in 1841.   He was the youngest of three sons, and was educated at Stock's Academy at Poplar.   Owing to his father's death, he left school at a very early age, and was placed in the office of a ship's broker.   Finding this work very uncongenial, he induced his relatives to article him to Carters and Green, builders of the famous China tea clippers, in the yard which subsequently became the headquarters of the Thames Ironworks and Shipbuilding Company.   His apprenticeship commenced at an unfortunate time, for wood was rapidly being replaced by iron in the construction of ships, and the old-established firms which did not move with the times were being left behind.   All the same, this period of his life must have been a particularly happy one.   He met all sorts of seafaring men, and in later life he never tired of relating anecdotes connected with their superstitions and adventures, and it is not unlikely that their experiences quickened

the sense of imagination which served him so well in after years. Shortly after completing his articles he married Mary, the daughter of John Cayzer, who organised the emigration to Australia of the East Anglian farm labourers in the starving 'forties and 'fifties. About this time he entered the service of Rickett Smith and Company, coal and coke shippers, as buyer. In this capacity he was brought in contact with the lime burning, plaster, and kindred industries, and when in 1876 a company was formed to work the bed of gypsum discovered four years earlier through the Sub-Wealden boring at Netherfield, Sussex, he took a small financial interest in the undertaking.   It was about this time that the necessity for technical education and scientific training was first accepted in England. In 1879 the City and Guilds of London Institute for the Advancement of Technical Education was formed, and almost immediately courses in chemistry under Armstrong in temporary premises in Cowper Street, Finsbury, were advertised. Although nearly forty years of age, Kemp, knowing that the manufacture of plaster at Netherfield rested entirely on rule-of-thumb methods, determined to take advantage of the facilities which the City Guilds Institute afforded and to become an efficient chemist. At Cowper Street he worked for one or two days a week, encouraged and inspired by Armstrong, and he soon proved himself to be not only a logical thinker, but an expert manipulator.   The other students in the laboratory were all boys, and the writer, who worked at the bench adjoining Kemp's, shared with them the admiration of his power of application and of his rapidly acquired skill. Kemp, influenced by Armstrong's spirit of research, soon began to make investigations on the production of sulphur from gypsum and from alkali waste, and these occupied him for several years. He was the first to suggest making alkali waste into a paste with water and pumping carbon dioxide into the sludge contained in an inverted conical vessel, thus making the gas do its own stirring and bringing every particle of the waste in contact with it. Some of the results of these investigations were subsequently embodied in Rawes's patents, which were worked by Chance.   During these years, the position of the Sub-Wealden Gypsum Company at Netherfield had become very critical, the output had fallen below 40 tons a month, the quality of the plaster was bad, and creditors were clamouring for payment of their accounts, which there were no funds to meet.   There was already on the bank an immense tonnage of dump, a grey stone considered useless, which had to be hauled to the surface with the white gypsum, and it was becoming increasingly difficult and expensive to dispose of it on the surface. A meeting was held with the object of winding up the company,

but Kemp, who had already begun to experiment with the grey stone, which consisted almost entirely of gypsum, persisted in the view that under proper direction the operations of the company would be successful. Two of the shareholders present were impressed, and agreed to provide further funds if Kemp would undertake the management, and it was thereupon decided that operations should be continued. Kemp's experiments with the grey stone were now pushed on, with the result that in a short time he had perfected a method whereby the waste was converted into a plaster of the Keen's cement variety, which, although dark in colour, set hard and evenly. He introduced this plaster under the name of "Sirapite," and from that day the success of the undertaking was assured. In 1891, 10 tons of "Sirapite" were sold; ten years later the annual sale was 15,108 tons, and in 1911 the sales exceeded 31,000 tons. Kemp's genius was shown not only in the way he attacked his problems on the chemical side, but also in his engineering ability and in the handling of men. From the first he recognised the inefficiency of boilers fed with water almost saturated with calcium sulphate, and within two years of taking control he had scrapped the steam plant and had substituted gas producers and large gas engines. He introduced kilns of large size, which reduced the consumption of fuel and greatly simplified the grinding and mixing plant. He subsequently opened up a new shaft in the mine, which he equipped with electric lighting and haulage plant. Having placed the business on a profit-earning basis, Kemp devoted his attention to the amelioration of the condition of his workpeople. Although himself prepared to work twelve hours a day or more, he reduced in 1895 the working hours to eight and afforded all workmen suitable opportunities for recreation. At his suggestion, the company built a large number of model houses standing in large gardens, which the workpeople were permitted to purchase at cost price. In 1903 Kemp completed his plans by bringing about an amalgamation of the chief makers of plaster in the United Kingdom.

Very few of those who travel by the South-Eastern Railway from Tunbridge Wells to Hastings realise that near Mountfield, hidden from, but within a few hundred yards of, the line, and in one of the most beautiful of the Sussex valleys, lie a mine fully equipped and busy works employing several hundred hands, at which a large part of the plaster used in this country is produced. It was here that Kemp conducted his experiments which revolutionised the industry, and it was here, at the scene of his life's work, that he breathed his last. Shortly after the outbreak of war his son, who for some years had assumed the management, volunteered for

service, and Kemp, then seventy-five years of age, returned to take charge. Always confident and cheerful, ever hard-working, he resumed his former duties with an activity and interest which might have been expected from a man thirty years his junior. On the morning of March 22nd, 1918, he rose in the usual health and spirits, but shortly afterwards, when about to go the round of the works, he suddenly expired. GERALD T. MOODY.

SYDNEY LUPTON.

BORN JANUARY 3RD, 1850; DIED JULY 10TH, 1918.

SYDNEY LUPTON, who was elected into the Society in 1872 and remained a Fellow until his death, was the youngest and last surviving son of Darnton Lupton and of his second wife, Anna Jane Busk. He was born at Eller Close, Roundhay, near Leeds, on January 3rd, 1850. His father, a member of a well-known Yorkshire family, was head of the firm of William Lupton and Co., woollen manufacturers. He was a man of considerable influence and public spirit, much respected, and took a leading part in the municipal politics and social life of the town and district.

His son, the subject of this notice, was educated at Rugby and lived in Dr. Jex Blake's house. From Rugby he passed to Oxford, where at Christ Church he came under the influence of Dr. Vernon Harcourt, and was led to devote himself to science, particularly to mathematics and chemistry.

On leaving the University, after taking his degree, he was appointed a science master at Harrow School. The work of school teaching was not uncongenial to him, and he had a fair measure of success in it; but his mother—now a widow—having fallen into indifferent health, he resigned his position in order to live with her at Harehills, near Leeds, where he established a small laboratory and continued to occupy himself with experimental work.

It was during this period that the writer of this notice made his acquaintance, and had the opportunity of observing the progress of his inquiry on the slow oxidation of potassium, the longest and perhaps the most important of his investigations. On the death of Mrs. Lupton he took a smaller house at Roundhay, where he continued to live until his removal to London in 1896.

During his residence in Leeds, Lupton took part in the civic life of the town, was a member of the Board of Guardians, and

was associated with the late Canon Jackson, Vicar of St. James's, in many charitable objects. For four years he was a member of the Committee of Management of the Cookridge Convalescent Hospital, and on his resignation, consequent on his leaving Leeds, his fellow-members recorded their appreciation of his genial and energetic help and their sincere thanks for his services "during a period requiring special administration." This last sentence has reference to the assistance he was able to render the institution in connexion with the erection of a wing to the building to perpetuate the memory of his friend, Canon Jackson.

Lupton's intellectual tastes led him to take an interest in the activities of the Leeds Philosophical and Literary Society, where he occasionally lectured on scientific subjects. He became a member of its Council in 1885–6, Honorary Secretary from 1886–95, and a Vice-President in 1895–6.

Practically the whole of Lupton's experimental work was done during his residence at Leeds. His first published paper, "On the Formula of the Alums," appears in the *Journal* of the Society for 1875. Although the doctrine of valency, which we owe to Frankland, was fairly well established at this period, there was considerable uncertainty as to the true formulæ of a number of inorganic compounds, owing to doubt as to the valency of particular elements. This was the case with the group of the alums. Lupton, at the suggestion of Dr. Vernon Harcourt, sought to establish the generic formulæ of these salts, independently of considerations of the combining values of their constituents, by a study of the conditions under which they lose their water on heating or on exposure to a dehydrating agent under reduced pressure, and he showed conclusively that they must contain at least twenty-four molecules of water, whence the general formula now universally accepted follows.

In the same year he published a note on the preparation of cuprous chloride, in which he described the different mode in which water acts on this substance, depending on its method of formation (*Chem. News*, 1875, **30**, 233). This was followed in 1876 by a number of short notices (*Chem. News*, 1876, **33**, 90). He showed that in preparing nitrogen by the well-known method of passing air over red-hot copper turnings, the operation might be rendered continuous by mixing the air with ammonia gas, whereby the cupric oxide was reduced as fast as it was formed, or, as is more probable, by the metal acting catalytically and inducing the production of water:

$$3(2N_2 + O) + 2NH_3 = 3H_2O + 7N_2.$$

R* 2

In this manner, only a relatively short length of heated copper turnings is needed, and the action proceeds uninterruptedly.

In another communication, on the "Solubility of Naphthalene in Water," he sought to disprove Garden's contention that Plateau's theory of the cause of the movement of this substance on the surface of water was invalid by showing that its solubility, and consequent high tension of its solution, are sufficient to account for the phenomenon.

He further described a number of reactions serving to distinguish aniline from naphthylamine, and made known a number of characteristic tests for succinic acid.

Lupton's most important chemical paper was his study of the "Slow Oxidation of Potassium," communicated to the Society in 1876 and published in the *Journal* for that year, in which he carefully repeated the observations of Davy, Berzelius, Gay Lussac and Thénard, and Harcourt, and sought to clear up certain discrepant statements with regard to the number of potassium oxides capable of existence. He confirmed Vernon Harcourt's work, made fourteen years previously (*Quart. Journ. Chem. Soc.*, 1862, **14**, 267), carefully watching the colour changes which follow the progress of the oxidation, and analysing the products at the several stages by a method he devised, and of which he proved the sufficiency. He was disposed to regard the existence of the grey suboxide, K_4O, of Berzelius as improbable, and he concluded that the intermediate products of oxidation were mixtures of K_2O and K_2O_2 in variable proportion, depending on temperature and time and the nature of the oxidising medium. He compared these intermediate products with the successive stages in the oxidation of lead and with the several lead oxides described by various observers, the general nature of the change being similar. He obtained analytical numbers for the yellowish-green product which corresponded with the composition of a dioxide, K_2O_2, and described a number of reactions which appeared to indicate its individuality. He gained no certain proof of the existence of the trioxide, K_2O_3, but was inclined to regard the brownish-yellow stage of the colour change as some evidence of its formation. He states that "the more thoroughly the air is dried, the less is its oxidising action," as proved by Baker (*Phil. Trans.*, 1888), and subsequently by Holt and Sims (T., 1894, **65**, 434), who showed that potassium may be distilled unaltered in perfectly dry oxygen.

Lupton's conclusions have been confirmed, in the main, by the last-named observers, although they found it impossible to associate the differences of colour with oxides of definite composition, the oxidation proceeding apparently without any break until the

heated mass consisted wholly of the bright orange-yellow peroxide, K_2O_4, described by Harcourt.

Holt and Sims also repeated Lupton's experiments on the action of the oxides of nitrogen on heated potassium, and with nitrous oxide obtained evidence of the formation of the buff-coloured trioxide and the sulphur-yellow dioxide, the existence of which in solution had already been established by Harcourt.

Lupton, in 1888, published a short communication in the *Proceedings* of the Society on compounds of chromium, and in 1891 he contributed to the *Philosophical Magazine* a controversial paper on "The Reduction of the Results of Experiments, with Special Reference to the Hydrate Theory of Solution" (*Phil. Mag.*, [v], **31**, 418), which produced a rejoinder from Mr. Spencer Pickering.

Sydney Lupton was a painstaking and conscientious worker, scrupulously accurate, and a good manipulator, cautious in drawing conclusions or in forming opinions, but very tenacious in holding them when convinced of their soundness. His knowledge and, as his published work shows, his sympathies were almost exclusively confined to inorganic and physical chemistry; and owing probably to the limitations of his early training and his subsequent lack of opportunity, he never seemed to be attracted by the problems of modern organic chemistry.

As a fellow-townsman and a member of the well-known Mill Hill Chapel, he was a great admirer of Joseph Priestley, who formerly ministered in Leeds, and began his chemical career there. At one time he conceived the idea of writing the life of the old philosopher and of bringing out an annotated edition of his complete works, for which he had gradually accumulated material. But to do justice to Priestley's astonishing versatility and the extraordinary range of his knowledge requires an equally exceptional man, and Lupton, after playing with the project for some time, finally relinquished it, being deterred from the attempt in all probability by its very magnitude. He was, however, well qualified to make it, especially as regards Priestley's scientific work and philosophical opinions, for he had considerable critical acumen and literary skill, was an omnivorous reader, and had extensive knowledge of the literature and science of the latter half of the eighteenth century.

On his removal to London, Lupton ceased to take any active part in experimental inquiry. He kept up his interest, however, in scientific work, was a frequent attendant at meetings of scientific societies, and at the lectures of the Royal Institution. He also interested himself in Bedford College, and in the work of St.

George's Hospital. and was for a time a member of its Committee of Management.

He was, perhaps, most generally known by his books on " Elementary Chemical Arithmetic " and " Numerical Tables and Constants in Elementary Science," published by Macmillan's, and based probably on his experience in science teaching at Harrow. His last production was a little book of some 120 small 8vo pages bearing the modest title, " Notes on Observations, being an Outline of the Methods used for determining the Meaning and Value of Quantitative Observations and Experiments in Physics and Chemistry, and for reducing the Results obtained." Notwithstanding the somewhat archaic ring of its title, it is an admirable piece of work. and well worthy of careful study by all engaged in quantitative work. In spite of its diminutive size, it must have involved a wide range of reading, no small exercise of criticism, and considerable skill and thought in arrangement and condensation. It shows Lupton at his best. It is a model of clear, restrained statement and rigorous logic, and should find a place in every physical and chemical laboratory.

At all periods of his life, Lupton was fond of travel, and his ample means made it easy for him to make extensive journeys. He was an acute observer and a shrewd judge of character, with a keen sense of humour—qualities which, added to his wide reading and knowledge of history and his readiness to communicate his knowledge, made him interesting as a companion.

He died at his London house, 102, Park Street, Grosvenor Square, on July 10th, 1918, and was buried at St. John's Cemetery, Roundhay. He showed his interest in the work of the Chemical Society by bequeathing to it his valuable chemical library.

T. E. THORPE.

GEORGE MARTINEAU, C.B.

BORN 1835; DIED FEBRUARY 5TH, 1919.

By the death of Mr. George Martineau, which occurred after a brief illness at his residence, Gomshall Lodge, Gomshall, Surrey, we have lost a member of an old and distinguished family and a man who was perhaps the greatest authority of his time in this country on sugar from its economic point of view. The deceased was the son of Mr. George Martineau, of Tulse Hill, and grandson of Mr. David Martineau, who in 1797 established the sugar refining firm which, as David Martineau and Sons, was at one time the largest in London ; it has remained in the family for more than a

century. The fact is not without interest to our Fellows that this firm was one of the first, probably the first, in this country to recognise the value of scientific control, and the partners appointed the late Mr. C. Haughton Gill, F.C.S., first as their chemist and subsequently as their manager.

Mr. Martineau was educated at University College, London, and on coming of age entered his father's business, in which he was actively associated until his retirement in 1896. His connexion with sugar refining was on the commercial side, but he always took a keen interest in the general technology of the industry. Although a Liberal of the Gladstonian school, he recognised the defects of our fiscal system more than forty years ago; and in 1872, when the effects of the foreign sugar bounties began to make themselves felt, the British refiners appointed a Committee with Mr. Martineau as Secretary. This Committee visited the principal beet-growing countries of Europe. Thus commenced the anti-bounty campaign, which culminated in the abolition of the bounties by the International Convention of 1902. In recognition of his services, Mr. Martineau was appointed a Companion of the Bath by King Edward VII.

Imbued with the true scientific spirit, Mr. Martineau possessed a thoroughly logical mind, clearly shown by his numerous writings, which were continued up to the last days of his life: it may be said, indeed, that he died in harness. He was a chemist by instinct, and few commercial men had a greater appreciation of chemistry and chemical research. Keeping himself *au courant* with all the chief events in the progress of our branch of science, it was doubtless with this object that he became a Fellow of the Chemical Society in 1871. It cannot be forgotten that, equally with those members of his firm connected with the practical side of sugar refining, he shared a strong belief in the precise methods which chemical analysis affords when applied to commercial questions. In this connexion, we may point out that he was a pioneer in the establishment of the Beetroot Sugar Association of London, the functions of which were to check the weights and make analyses of the whole of the raw beetroot sugar shipped from the Continent to the Port of London.

Mr. Martineau's memory will be cherished by many. His charming personality, gifted conversational powers, wide erudition, and his deep sincerity had secured for him a wide circle of friends. Not a few have reason to be grateful to him for the assistance and encouragement he gave them at the commencement of their careers; but from these he resented open thanks, being quite content to view their progress with silent satisfaction.

ARTHUR R. LING.

SIR ALEXANDER PEDLER, F.R.S.

BORN MAY 21ST, 1849; DIED MAY 13TH, 1918.

LIKE many other chemists who have attained an eminent position in the scientific world, Pedler began life in connexion with pharmacy. His father, Mr. George Stanbury Pedler, was in business as a pharmacist at 199, Fleet Street until, on the removal of old Temple Bar and the widening of Fleet Street, preparatory to the erection of the Law Courts, the premises were swept away.

Pedler received his early education in the City of London School, which he left at midsummer, 1865. In October of the following year, at the age of seventeen, he won a Bell Scholarship, and began work as a student in the laboratory of the Pharmaceutical Society in Bloomsbury Square. Here he went through the usual course of analytical work, and at the end of the session he was awarded a certificate of honour in practical chemistry. Before leaving, he began a piece of research suggested to him by the present writer, who was at that time Demonstrator in the laboratory. It was with great regret that he parted with the promising young student, who by this time had decided to leave the comparatively narrow field of pharmacy and proceeded to place himself under Professor (afterwards Sir Edward) Frankland, at the Royal College of Chemistry, then in Oxford Street. There, after carrying on his studies for two years further, he assisted Frankland in the separation of the amyl alcohols of fousel oil by Pasteur's process. This work was done in the laboratory of the Royal Institution, where Frankland had held the Professorship of Chemistry in succession to Faraday since 1863. From the optically active and inactive alcohols, Pedler prepared the corresponding valeric acids, and gave an account of his work to the Chemical Society in 1868 (*Journ. Chem. Soc.*, **21**, 74). Further work in this direction was interrupted by his taking part in the solar eclipse expedition to Sicily in that year.

From 1871 Pedler served for two years as lecture demonstrator to Sir Edward Frankland in the Royal College of Chemistry in succession to Mr. Herbert McLeod, who had been appointed to the professorship of chemistry in the then newly instituted Royal Engineering College at Cooper's Hill. At the same time, he assisted in the research work on gaseous spectra in which Frankland and Lockyer were jointly occupied. This naturally directed Pedler's attention to the fascinating problems connected with the physical constitution of the sun and the stars. Consequently, on receiving

in 1873 appointment as professor of chemistry in the Presidency College, Calcutta, he naturally occupied himself with subjects connected with celestial chemistry, and soon after his arrival in India he was charged with special duty in connexion with the eclipse expedition of 1875.

On joining the Presidency College, he found that no practical work in any department of science was done by the students. To remedy this deficiency in the scheme of instruction was his first care, and ultimately he succeeded in securing the introduction of a small amount of practical work into the science course for the M.A. degree, and a practical examination was held for the first time in 1882. Ultimately, he had the satisfaction of finding the university regulations require every college sending up students to provide the necessary staff and appliances for teaching practically each of the departments of science, and each candidate for B.A. or B.Sc. degree to be examined practically.

Having been born in 1849, Pedler was still a very young man on reaching India, and those who knew him in his early days will gladly recall those features of his character which made him not only popular in youth, but, remaining unchanged to his latest years, contributed materially to his success in official life.

In India Pedler retained the professorship in Calcutta, together with the office of Meteorological Reporter to the Government of Bengal, for twenty-two years. He then became Principal of the Presidency College and Vice-Chancellor of the University. In 1899 he was appointed Minister of Public Instruction in Bengal, and became an additional Member of the Legislative Council under the Viceroy.

Among other institutions, Pedler took great interest in the Ravenshaw College at Cuttack, and was instrumental in obtaining accommodation for the physical and chemical departments in that institution. These successive steps in official life explain the fact that Pedler's original contributions to scientific chemical literature were limited to the one paper on valeric acids, already mentioned, and several which arose out of the circumstances of his residence in India.

Soon after his arrival in that country, he examined and reported on the coal-gas and water supplies of Calcutta. In 1878 he sent home a paper on the poison of the cobra, which was printed in the *Proceedings* of the Royal Society (**27**, 17).

In 1890 he contributed to the *Journal* of the Chemical Society three papers, which showed that he was utilising opportunities, previously neglected by chemists, of studying the action of tropical sunlight on chemical change. The first of these papers was entitled

"The Action of Light on Phosphorus and some of the Properties of Amorphous Phosphorus." The second paper was on "The Action of Chlorine on Water in the Light, and the Action of Light on certain Chlorine Acids." The third paper contained an account of attempts to estimate hydrogen sulphide and carbon bisulphide in gaseous mixtures by explosion with oxygen.

Pedler was a Fellow of the Institute of Chemistry and of the Chemical Society. He was elected F.R.S. in 1892. He was also an honorary member of the Pharmaceutical Society.

In recognition of his public services in India he was created C.I.E. in 1901, and on his return to England in 1906 he received the honour of knighthood. On his retirement he soon found occupation in public work; he became honorary secretary to the British Science Guild, which owes much to his devoted service, and on the outbreak of war he took up active duties connected with the research department of the Ministry of Munitions. Whilst attending a meeting of Committee at that office on Monday, May 13th, 1918, he was seized with sudden illness and expired immediately. His death came as a great shock and surprise to his many friends, among whom no suspicion of weakness had been entertained.

Pedler was twice married, first in 1878 to Elizabeth Margaret, daughter of C. K. Schmidt, of Frankfurt, and, secondly, to Mabel, youngest daughter of the late Mr. W. Warburton, R.N., of Dedham, who survives him. He left no children.   W. A. T.

JOSEPH PRICE REMINGTON.

BORN MARCH 26TH, 1847; DIED JANUARY 1ST, 1918.

JOSEPH PRICE REMINGTON was born at Philadelphia on March 26th, 1847, and belonged to a well-known Quaker family, his ancestors having been for three generations members of the Society of Friends. His father, Dr. Isaac Remington, was a prominent Philadelphia physician, whilst his mother, the daughter of John Hart, was in a direct line of descent from an apothecary who practised his art in Philadelphia early in the eighteenth century. An inclination for the professional pursuit of pharmacy, which was manifested by Remington at an early age, would thus seem to have been inherited.

At the comparatively early age of fifteen years, Remington

suffered the loss by death of his father, and this appears to have affected his subsequent career; for a plan to supplement his preliminary education—obtained in private schools and in the high school at Philadelphia—by an academic course of study had to be abandoned. In 1863 he entered the establishment of Charles Ellis, Son and Co., a firm of wholesale druggists in Philadelphia, where he remained for four years, and during that time he attended evening lectures at the Philadelphia College of Pharmacy, from which he graduated in 1866. During the years from 1867 to 1870 Remington was employed in the manufacturing laboratories of Dr. E. R. Squibb, at Brooklyn, N.Y., and in this position he had exceptional opportunities for acquiring a knowledge of technical methods, especially in their application to chemical and pharmaceutical products, whilst also enjoying intimate association with a man who was widely known for his scientific attainments and exceedingly high ethical standards. Remington then returned to Philadelphia, and after a short period of service with the firm of Powers and Weightman, manufacturing chemists of that city, he established a pharmaceutical business on his own account, which was successfully conducted for thirteen years. In the meantime, he had also served as an assistant to Professor Parrish, and subsequently to Professor Procter, at the Philadelphia College of Pharmacy, and on the decease of the latter, in 1874, he was elected to the professorship of pharmacy in the college which had been his *alma mater*. The position which Mr. Remington was thus called on to fill he retained for the exceptionally long period of fortyfour years, or until the close of his life, and during that time several thousand students had received instruction from him.

As circumstances did not permit Professor Remington to acquire a scientific training, in the modern sense, his attainments and talents were directed more to what may be termed the practical side of pharmacy and to editorial work. As examples of this activity, there may specially be noted his participation in several revisions of the " United States Dispensatory," the publication of his well-known text-book, entitled the "Practice of Pharmacy," and the arduous duties committed to him as Chairman of the Committee of Revision of the " United States Pharmacopœia."

Professor Remington was a Fellow of the Chemical, Linnean, and Royal Microscopical Societies of London, as well as an active member of several scientific societies in his own land. The esteem in which he was held by his professional colleagues had, moreover, been manifested by the bestowal of honorary membership in a large number of pharmaceutical organisations both at home and abroad. He had travelled widely in his own country, and had

several times visited Europe, the last occasion having been in the autumn of 1913, which will still be pleasantly remembered by many of his English friends.

The home life of Professor Remington, with a devoted wife and several children, was particularly happy. His genial nature and fluency as a speaker, together with the fund of interesting information which he possessed, rendered him a most pleasant companion. In social as well as professional circles he was therefore always gladly seen, and accorded a prominent place.

The writer of these lines is grateful for the privilege of rendering a slight tribute to the memory of one with whom a friendship had been sustained for more than forty years, and whose qualities of mind and heart had won such extended appreciation and regard.

F. B. POWER.

JEAN JACQUES THÉOPHILE SCHLOESING.

BORN JULY 9TH, 1824; DIED FEBRUARY 8TH, 1919.

ONE of the oldest and most distinguised of the foreign members of the Society, Jean Jacques Théophile Schloesing, passed away on February 8th of this year. He was in his ninety-fifth year, and almost all his life had been associated with agricultural chemistry. He knew its illustrious founders, Boussingault, Lawes, and Gilbert, when they were still young men almost at the beginning of their careers; he introduced new ideas at a critical stage, and, finally, when development had temporarily ceased, he opened up a new path, which is still leading to fruitful results.

Schloesing was born at Marseilles on July 9th, 1824. At the age of seventeen he entered the Polytechnic School, and left it two years later to take a post in the " Service des Manufacteurs d'Etat." He thus began his career at the most eventful period in the history of agricultural chemistry; it was the year, 1843, in which Lawes and Gilbert started their great work at Rothamsted, one year after Liebig's famous report on agricultural chemistry to the British Association, and four years after Boussingault had commenced his striking investigations at Bechelbronn.

He must have done well in his first post, for three years afterwards—in 1846—he became Director of the École des Tabacs, and within a few months published his first paper in the *Comptes rendus*; it was on nicotine and its estimation in leaf and manu-

factured tobacco. He was the first to obtain nicotine in any quantity; it had previously been prepared, as he tells us, only in "quelques rares échantillons." Schloesing verified its composition and designed a method for estimating it within about 1 per cent.—a very accurate determination for the time. The method consisted in displacing the nicotine with ammonia, extracting with ether, eliminating the excess of ammonia by the evaporation of the ether, and then titrating the residual base with sulphuric acid. For five years no further publications appeared, then followed an ingenious paper on the determination of ammonia in tobacco; milk of lime was added, and the mixture placed over sulphuric acid in the cold. The ammonia volatilised, and was absorbed by the acid, but at the low temperature of the experiment no decomposition of other substances occurred. This paper was followed shortly afterwards by one on the estimation of nitrates in presence of organic matter; hydrochloric acid and a ferrous salt were added, and nitric oxide produced; this was washed free from hydrochloric acid, then mixed with air or oxygen, converted into nitric acid, and titrated with an alkali. Subsequently, however, Schloesing found that conversion into nitric acid was unnecessary, and he designed a method for direct measurement of the nitric oxide. He also introduced considerable improvements into the methods for estimating ammonia in dilute liquids, such as rain. As an illustration of the very cumbersome nature of some of the methods then in vogue, it may be mentioned that the determination of ammonia in rain-water at Rothamsted, carried out in 1853, had involved the distillation of 2 cwt. of rain and evaporation of the distillate with sulphuric acid; in spite of all the laborious care bestowed on the work, the figure obtained was probably double the true value.

For the next seven years Schloesing published no scientific work, but from 1860 onwards he issued a number of important publications. In 1860, also, he began some cultural experiments with tobacco, which lasted for fifteen years, and were designed to ascertain whether the physical properties and nicotine content of the leaf are characteristic of the variety or the result of environmental factors. In the first series, tobacco was raised from samples of seed coming from various regions; the resulting leaf had in each case the physical characters and nicotine content characteristic of the parent plants grown in their original home. The second series was more extended and lasted fourteen years; its purpose was to discover whether any marked alteration occurred in the characteristic properties when a variety is cultivated in a new district. Havanna tobacco was grown, and the seed saved; some was sown and some was stored; each year a certain quantity of the seed of

each generation was sown. In no case was any difference observed.

In 1866 Schloesing began his investigations on the soil. It was probably in this subject more than in any other that the genius of the man shone out. Looking back at these papers, their striking feature is their modernness; one can well believe that at the time of publication they would not be fully appreciated. Again and again he broached new subjects, which neither he nor his contemporaries developed, but which later workers rediscovered thirty or forty years afterwards and showed to be of signal importance. He was essentially a pioneer rather than a builder, and he had the extraordinarily good fortune to discover gold almost every time; but he never himself developed his "finds," and the subject was not sufficiently well organised to ensure that others should develop them for him.

Schloesing's period of greatest activity was from 1866 to 1879, when he was between forty-two and fifty-five years of age; during this time he opened up no fewer than five new fields of soil investigation, three of which are now proving extremely valuable. His first soil paper was on the soil solution, which he separated from the solid particles by a displacement method. The subject received very little attention for nearly forty years; its importance was not fully realised until Whitney and Cameron in America published their striking paper in 1903, when investigations began again, using at first methods similar to those that Schloesing had designed. At the present time it receives perhaps more attention than any branch of soil chemistry.

Another subject which has come into prominence in recent times was investigated by him in 1868. He showed that nitrates are decomposed during certain fermentations, and five years later he further showed that they are reducible to gaseous nitrogen in soils deprived of oxygen. He also demonstrated that oxidations rather than reductions are the normal phenomena in soils under natural conditions; surface soils readily absorb oxygen, whilst sub-soils do not. After a lapse of nearly thirty years this phenomenon was independently rediscovered, and its investigation figures prominently in some of the most recent research programmes.

His most important work, however, was on nitrification. For a long time it had been known that nitrates are gradually formed when plant or animal residues, farmyard manure, etc., are incorporated in the soil. The process was of much technical importance in the seventeenth and eighteenth centuries as the source of nitrates for gunpowder. During the Thirty Years' War and other great continental wars, the various governments had been seriously

concerned in these so-called nitre beds, and had done a great deal to stimulate their development. An interesting collection of memoirs relating to the practical details was published in Paris in 1776.* A study of these papers shows that the conditions of the change were tolerably well ascertained even then, but nothing was known of its mechanism.

It has several times happened in the history of civilisation that agriculture has benefited by knowledge gained during war. The mass of information accumulated during the eighteenth century wars, and apparently rendered useless in the nineteenth century by the promise of peace and the discovery of nitrates in Chile, was found to be of fundamental importance in agriculture. Boussingault had realised, and Schloesing at once accepted the view, that the nutrition of plants, so far as nitrogen was concerned, depended on the nitre-bed processes; organic nitrogen compounds, useless as plant nutrients, became converted into highly valuable nitrates when added to the soil; the more rapidly this change could be brought about, the better for the plant. So long, however, as the mechanism of the change was unknown, the old knowledge was simply empirical and incapable of full utilisation. Many investigations had been made, but the problem remained unsolved. The balance of opinion was in favour of a purely physical process, but there was also a strongly supported chemical hypothesis.

In 1875 a Commission was appointed to inquire into a scheme for carrying Paris sewage out to the land between Clichy and the forest of St. Germain, and Schloesing was asked to draw up the report. Rarely, even in France, can an essentially practical inquiry have led to such striking scientific results. When Schloesing had finished the investigation, he had not only discovered a new and vastly improved method of treating sewage, but he had realised what was the cause of nitrification, and thus founded the science of soil bacteriology. We cannot do better than let him tell the story in his own words:

"I was selected," he tells us, "to draw up the report of this Commission. On this occasion, following the plan indicated in 1856 by M. Hervé Mangon, and taking advantage also of the more recent investigations of Dr. Frankland, I endeavoured to elucidate the principles involved in the land treatment of sewage by connecting the process with the phenomena of slow combustion of organic matter in an atmosphere containing oxygen; I investigated at the same time the conditions necessary to secure satisfactory

* "Receuil de Mémoires et d'Observations sur la formation et sur la fabrication du Salpètre par les Commissionnaires nommés par l'Académie pour le jugement du Prix du Salpètre."—Paris, 1776.

purification in practice. I made a special point of distinguishing two problems which were often confused: purification simply and solely of Paris sewage, which would only require an area of 2000 hectares (5000 acres), and agricultural utilisation of Paris sewage, which would require an area twenty times as great.

"Boussingault had just published the researches on nitrification that he had carried out some time previously. Blood, meat, wool, straw, and oil-cake did not nitrify when mixed with sand and chalk and allowed slowly to oxidise, but they rapidly nitrified when mixed with soil. I had vainly tried to nitrify ammonia by adding it to sand and chalk and leaving the mixture exposed to air. These results led me to think that the property of bringing about nitrification was peculiar to soil.

" Wishing to fix my ideas on the subject, I made the following experiment. A large tube, 1 metre long, was filled with 5 kg. of ignited sand mixed with 100 grams of powdered chalk. The sand was watered daily with sewage, the amount being so arranged that it took eight days to traverse the tube. For the first twenty days there was no sign of nitrification, then nitrates began to appear, and the amount rapidly increased; finally, the liquid flowing out of the tube contained neither ammonia nor organic matter—the sewage was absolutely purified."

The quality of the man's genius was revealed in two striking deductions drawn from this simple experiment. One was of supreme practical importance, and has revolutionised sewage disposal practice.

"Au point de vue de l'épuration des eaux d'égout, l'expérience . . . prouve, en effet, qu'il n'est nullement nécessaire que l'irrigation soit établie sur les terrains agricoles; de sables steriles se prêtent parfaitement à l'épuration, lorsque le ferment nitrique, apporté par les eaux mêmes, a pris possession du milieu."

From this to the modern bacteria bed is no great step, at any rate in principle.

The second deduction was of even greater consequence for the development of agricultural science. Reverting to the delay of twenty days in the setting in of nitrification, Schloesing and Muntz asked why it set in. With characteristic shrewdness they observed that this delay could scarcely arise if the process were purely physical or chemical; some biological factor seemed to be indicated. In order to test this possibility they added a little chloroform to the sewage; nitrification at once stopped. They then removed the chloroform and "seeded" with a little fresh sewage; after an interval nitrification began again. This showed that the process was brought about by living organisms, and forthwith Schloesing

and Muntz announced the existence of a living ferment. The discovery at once attracted attention; Warington at Rothamsted immediately recognised its importance, and proceeded to investigate nitrification in the Rothamsted soils; he was able to confirm the accuracy of Schloesing's deductions. Later on, the proof was made more rigid by Winogradsky's discovery of the organism. It is no diminution of the credit of the discovery that Pasteur in 1862 had already foreshadowed it, as Schloesing himself pointed out, in his remarkable statement:

"Beaucoup d'êtres inférieurs ont la propriété de transporter l'oxygène de l'air, en quantité considérable, sur les matières organiques complexes: c'est un des moyens donc se sert la nature pour transformer en eau, acide carbonique, oxyde de carbon, azote, acide nitrique, ammoniaque, les éléments des substances organiques élaborées sur l'influence de la vie."

This research marks the beginning of soil bacteriology. It seized the imagination of the younger workers, and speedily attracted recruits to the new subject. Although Schloesing did not himself develop the subject, he was satisfied that the "ferment nitrique" did not exhaust the list of soil organisms. Reverting to his earlier work on the absorption of oxygen by soils, he says in one of his lectures*: "C'était là, pensait-on alors, un fait purement chimique. On sait aujourd'hui que c'est principalement un fait biologique, c'est-à-dire que la combustion observée est le résultat de la vie de nombreux organismes, tel par example que le ferment nitrique, lequel est chargé de transporter l'oxygène sur l'azote."

These investigations by no means represent the whole of his work on soil, although they may well prove to be his most permanent contributions to science.

By a lengthy washing process, he obtained a preparation of the finest clay particles which remained indefinitely suspended in pure water, but was precipitated by traces of a calcium or magnesium salt. This was commonly regarded as being in some sense the essential clay, and agricultural chemists marvelled at the minute amount present even in heavy soils. The conception served a useful purpose, but it has since been replaced by a broader one: the soil is now considered to be made up of particles varying from 1 mm. downwards to molecular dimensions, the different groups merging one into another without perceptible breaks. The clay group is assigned for convenience an upper limit of 0·002 mm., but this is regarded as purely conventional.

Another important investigation had to do with the movements of calcium carbonate in the soil. The conditions of solubility of

* "Leçons de chimie agricole," 1883.

calcium carbonate in carbonic acid were determined, and the relationship between the quantities of these two substances was shown to follow a logarithmic law. Deductions were drawn which threw important light on the practice of liming and marling, and on the presence of lime in natural waters.

During the course of these investigations, Schloesing was appointed in 1876 to the Chair of Agricultural Chemistry in the Institut Agronomique, then just founded. Eleven years later, in 1887, he followed the illustrious Boussingault at the Conservatoire des Arts et Metières. During his active period, his lectures were collected by his son in a volume, which still remains a source of inspiration to the student.

In 1875 he began another important group of investigations: he carried out a series of determinations of the amount of ammonia in the air, and published some interesting speculations as to its source. He supposed that a great natural circulation took place; the nitrates washed out from the soil find their way to streams and rivers, and finally to the sea; there they are reduced to ammonia, some of which escapes into the atmosphere, is blown over the land, and there absorbed by the soil or washed down by the rain. The ammonia then nitrifies, and such of the resulting nitrate as is washed out from the soil by rain-water passes once more through the same cycle.

In like manner, he supposed a circulation of carbon dioxide between oceans and atmosphere, and in this way he explained the smallness of the variations in amount of the carbon dioxide in the air from time to time. He considered that the proportion of carbon dioxide in the air was probably diminishing, although, of course, very slowly. "What," he asked, "will be the result?"

"Cet appauvrissement continue-t-il encore, et, s'il en est ainsi, ira-t-il jusqu'au point où il causerait la ruine de la végétation et par suite la fin de toute vie à la surface de la terre? La solution de cet problème d'un si haut intérêt nous échappe absolument. Elle ne pourra être donnée que par les générations qui viendront longtemps après nous."

Well may we envy a man and a generation that had nothing worse to worry about!

<div style="text-align: right">E. J. Russell.</div>

ALFRED SENIER.

BORN JANUARY 24TH, 1853; DIED JUNE 29TH, 1918.

I.

ALFRED SENIER was born on January 24th, 1853, at Burnley, in Lancashire. His father, who had been one of the early settlers in Dover, Wisconsin, had returned to England some six years previously to engage in business as a pharmacist, but for reasons of health he found it necessary to return to America shortly after the birth of Alfred, his eldest son. Thus except for a brief visit to England during infancy and another during his student days, Senier's whole youth up to the time of his graduation as M.D. at the University of Michigan in 1874 was spent in the United States, chiefly at Mazomanie. Mr. Alfred Senier, the father, appears to have been a man of romantic disposition, which found its expression in a certain restlessness, leading him in early life to spend several years at sea and later to travel considerably in Europe. The son inherited this taste for travel, and was allowed to visit both London and Paris at the age of eighteen in the middle of his student career.

Immediately after his graduation the family finally returned to London, where Senier obtained a post at the school of the Pharmaceutical Society, first as assistant to Prof. Attfield and later as demonstrator. He was elected a Fellow of the Chemical Society in 1875 and a Fellow of the Institute of Chemistry three years later.

In 1881 he left the school of the Pharmaceutical Society in order to take charge of the chemistry teaching at St. John's College, Battersea, where he remained for three years.

During this period in London his interests extended beyond his professional duties, which hitherto did not seem to offer him sufficient scope for his mental activities. Endowed as he was with the faculty of accurate reasoning, and with clearness and breadth of mental vision, his interest at this time turned markedly to philosophical questions. We find him appointed as honorary secretary and treasurer of the Aristotelian Society on April 19th, 1880, when it was first organised. He acted in this capacity until 1884, and in 1902 he was elected an honorary life member. At its fifth meeting he delivered a lecture to the Society on "Plato." In 1882 we find him delivering a series of lectures on the "Elements and Early History of Terrestrial Physics" to the Positivist Society in Newton Hall, Fetter Lane. It is also interesting to observe that he wrote to the *Pharmaceutical Journal* in 1877 a spirited letter in

support of the proposal to admit lady pharmacists into the Pharmaceutical Society.

In 1884 he left London for Berlin, where he studied chemistry under A. W. von Hofmann. It was at this period of his life that he received his greatest inspiration. Enthusiastic and imaginative by nature, he threw himself wholeheartedly into his work, and soon attracted the attention of Hofmann, who became his ideal as a professor, lecturer, and teacher. A close friendship bound him to his old master, in whose family circle he spent many happy evenings, and whose personality made a lasting impression on his mind.

Later in life when fulfilling his duties in an academic chair he loved to think that the same happy relations existed between his students and himself as he had felt when a student of Hofmann. His interest in his past students never flagged. He was ever ready to help them, and always pleased to hear of their success.

Senier's own exceptional powers as a teacher were no doubt due to a large extent to the powerful influence of Hofmann, of whom he was never tired of speaking. Among his papers this idea is expressed in words thus: " I had special opportunities for studying the methods of teaching for which Hofmann was justly famous. He possessed that rare gift of inspiring his students with the discoverer's enthusiasm. We discovered, with him to lead us, things known to science; and then, without realising a difference, we followed him to things that were new, and thus became chemists with the habit of research. With such a leader in research, with such a teacher in the right meaning of the word, no wonder that those who came within his influence became inquirers and teachers too."

On June 25th, 1887, he graduated Ph.D. in Berlin, and returned shortly afterwards to London.

Here he remained for a few years writing articles for the standard dictionaries of chemistry until he was called to act as locum tenens for Maxwell Simpson, Professor of Chemistry at Queen's College, Cork, in 1890. The latter resigned the following year, and was succeeded by Prof. A. E. Dixon, of Galway. The vacancy thus created was filled by the appointment of Senier to the Chair of Chemistry at Galway, which he occupied until his death.

This Chair when first established in 1849 was filled by Edmund Ronalds, who in the early days of the Chemical Society served as Secretary and also acted as Editor of this Journal.

In addition to fulfilling the duties as Professor of Chemistry at Queen's College, Galway, Senier acted as Lecturer in Medical Jurisprudence and Hygiene.

In Galway his professorial duties, his work on the College Coun-

cil, and his personal interest in his students engaged his closest attention. His strong personality and buoyant enthusiasm made a powerful appeal to the minds of his students, with whom he was always immensely popular. He was a champion of students' interests, and never tired of reminding them that he was, and would remain, "always a student." Although not naturally attracted to athletic sports, he quickly realised their healthy influence and value in promoting *esprit de corps* and harmony among young men, assembled from all parts of Ireland, from homes representing all shades of religious and political differences. They sought and obtained in Galway a University training under a system which, although technically non-residential, was by reason of the smallness and isolation of the " Citie of the Tribes" virtually residential. Senier seized his opportunity and quickly won the affection of all the students by becoming the active patron of their sports. He founded the athletic union and acted as its president and treasurer for seventeen years. The astonishing prowess of the football team in its competitions with the larger sister colleges of Belfast and Cork was in no small measure due to his sympathetic and generous support.

Meanwhile, the problem of continuing his researches had to be faced, and was tackled courageously and successfully. At first little progress could be made, as Galway offered but a poor field for creating and maintaining an advanced chemical atmosphere. Nevertheless, he persisted in his attempt, and soon acquired a good chemical library and equipment sufficient to make a start. Well-furnished modern laboratories soon followed, and in conjunction with various assistants, demonstrators, and senior students he was eventually able to contribute a large number of papers, chiefly on acridines and on phototropic and thermotropic compounds, to the *Transactions* of this Society.

In 1908 the Royal University of Ireland conferred on him the degree of D.Sc. *honoris causa*. This event was made the occasion of a public presentation to him of an address and silver casket from his old students, whose eager and liberal response, even from the most distant parts of the world, bore ample testimony to the lasting feeling of reverence and goodwill in which they held their old teacher and patron of their sports.

He was elected a member of the Royal Irish Academy, and in 1912 he acted as President of the Chemical Section of the British Association at the Dundee Meeting.

When the National University of Ireland was created in 1908 he took an active part in its organisation and development. He was

a member of the Senate until his death, which took place on June 29th, 1918, in Galway after a brief illness. Senier married in 1887, and is survived by his wife and two daughters.

W. S. M.

II.

By the death of Alfred Senier the country has lost one of its most enthusiastic and devoted workers in the domain of organic chemistry. The loss is felt most keenly by all his students and co-workers, who will always cherish the remembrance of his sympathetic and inspiring personality. In him the spirit of scientific inquiry was strong indeed, for in the face of difficulties, which would have baffled and beaten many a man of less sterling worth, his courage never failed, but enabled him to pursue unwearyingly the lofty ideals which he had formed in his youth and to achieve a measure of success and distinction which will assuredly become fruitful in the future.

Even before leaving America he had shown evidence of a desire to undertake original investigations, his first paper, on the analysis of soap, appearing in the *American Journal of Pharmacy* in 1874. At the School of the Pharmaceutical Society his aspirations received encouragement from Prof. Attfield, and he contributed a series of articles to the *Pharmaceutical Journal*, chiefly relating to the investigation of pharmaceutical preparations and including a table for the qualitative analysis of scale preparations, alkaloids, etc. The interaction of glycerol and borax particularly engaged his attention, because he found that he could utilise it as a means for detecting glycerol. In 1878 he contributed to the *Transactions* of the Chemical Society "A New Test for Glycerin." He also published a number of articles in the *Sanitary Engineer*.

In Berlin Senier came under the powerful influence of A. W. von Hofmann. The enthusiasm which Hofmann aroused in him remained with him to the end, and he spoke of him almost with veneration in his public lectures.

Inspired as he was by his experience in Germany, the whole course of Senier's later life afforded abundant evidence that he had learned nothing of the modern German aggressive spirit of world-domination. Indeed, his realisation of its existence only came to him after war was declared, and its effect on him was painful in the extreme, as shown in his letters to the writer.

In Berlin his attention was first directed to the action of heat on the formyl and thioformyl derivatives of aromatic amines, and later to the investigation of cyanuric acid and cyanuric chloride. He was

able to show that the alleged α- and β-isomerides obtained by Herzig by the interaction of carbamide and hexabromoacetone were in reality identical with ordinary cyanuric acid. This work was embodied in his dissertation for the degree of Ph.D.

Shortly after his appointment to Galway he reverted to the examination of cyanuric acid, and found that the white solid produced by the polymerisation at 0° of freshly distilled cyanic acid was not pure cyamelide as was supposed, but consisted chiefly of cyanuric acid mixed with 30 per cent. of cyamelide.

Being greatly interested in all Hofmann's work, he decided to follow up the reaction by which ethylenediamines and piperazines are formed from arylamines. By using methylene dihaloids instead of ethylene dihaloids, he found that although the simplest arylamines give rise to methylenediamines, as the molecules increase in complexity through the inclusion of methyl groups or of condensed rings, the character of the reaction changes and results in the formation of acridines. Thus from ψ-cumidine he obtained hexamethylacridine, and from α-naphthylamine a new dinaphthacridine. This result led him to study the subject of acridines in some detail, and a series of papers appeared in the *Transactions*. He also introduced a new and convenient system of notation in the acridine series. This work was followed by a paper on quinazolines and a series of papers on the synthesis of phototropic compounds, to which he was led by his observations on salicylidene-*m*-toluidine during the course of his investigations on acridines. This discovery of phototropic change led him to prepare and examine a large number of similarly constituted anils, many of which were also phototropic, although the property was by no means characteristic of the class. The change from the paler variety to the darker under the influence of sunlight occurs rapidly in a few minutes—whereas the reverse change requires a much longer time. This process of reversal can, he found, be accelerated by raising the temperatures, but there appears to be for each substance a critical temperature above which the property of phototropic change disappears. In some cases this temperature is near the melting point; in others it is much lower; in fact, in the case of two compounds examined, namely, salicylidene-*p*-anisidine and 2-hydroxy-3-methoxybenzylidene-*p*-xylidine, no phototropic change is observed until a temperature of −20° is reached. Similar colour changes were observed to take place under the influence of heat instead of light, this phenomenon being termed *thermotropy* by Senier. Thermotropy appears to be much commoner than phototropy, and in many instances the thermotropes were also found to be phototropic. The suggestion was put forward by Senier that these phototropic and thermotropic

changes are to be ascribed to isomeric changes affecting the aggregation of molecules in solids rather than to changes in the structures of the molecules themselves. In his Presidential address to Section B of the Dundee meeting of the British Association in 1912 he developed this idea of the existence of solid molecular aggregates. Several instances of polymorphic changes due to trituration were also examined, chiefly in the case of p-hydroxybenzylidenearylamines. This work, extending over several years, was the subject of a series of papers in the *Transactions*, and remains unfinished. No doubt it will be possible in the future to throw more light on the subject by means of optical measurements.

Apart from his purely scientific studies, Senier took a deep interest in educational affairs. The difficulties which had to be encountered in Galway were due partly to the remoteness of the College from the main centre of scientific activity and partly to the anomalous character of the College during the greater part of Senier's life in Galway.

Since the dissolution of the Queen's University in 1879 the three Colleges at Belfast, Galway, and Cork had been reduced from the status of integral members of a university to that of colleges where students were able to study for the examinations of an external institution—the Royal University. In addition to this loss of prestige, the College at Galway suffered through lack of active support by the people of Connaught. It was therefore not in close sympathy with its environment. This state of affairs has happily been remedied by the abolition of the Royal University and the creation in 1908 of two new teaching universities, namely, the National University of Ireland and the Queen's University of Belfast. The College at Galway, re-named "University College, Galway," became a constituent part of the National University, and Senier was elected to a seat on the Senate. The existence of the College has often been threatened, but it has survived and, indeed, attained a flourishing condition. There is no doubt that Senier's efforts to foster the spirit of scientific research materially advanced the cause of education in Galway and in Ireland. In his public lectures on "A Visit to Giessen; or Thoughts on Liebig and Chemistry in Germany" and "Bonn on the Rhine; Pages from its History and Stray Thoughts on Education" he deals in a very attractive way with the history of the development of scientific research in Germany, and in his lecture before the Royal Dublin Society in 1910 on "The University and Technical Training" he made a very lucid and careful analysis of the various university systems in the world. In view of modern needs these essays * are

* Published at Dublin, 1910, by Edward Ponsonby, 116, Grafton Street.

well worth reading, for he explains very clearly how industrial development does not depend on the technical education of the operatives, but arises naturally from the development of the highest form of scientific activity at the universities.

<div align="right">P. C. AUSTIN.</div>

JOHN BISHOP TINGLE.

BORN 1867; DIED AUGUST 5TH, 1918.

JOHN BISHOP TINGLE, Professor of Chemistry in McMaster University, Toronto, who died on August 5th, 1918, at the age of fifty-one, after a brief illness, received his early training at the Royal Grammar School, Sheffield, entering Owen's College, Manchester, in 1884, under the late Sir Henry Roscoe. In 1887 he proceeded to the University of Munich to study with Claisen and von Baeyer, where he took the degree of Doctor of Philosophy in 1889. While at Munich his studies were essentially in organic chemistry, his dissertation for the degree dealing with the action of ethyl oxalate on aliphatic ketones.

On returning to England Dr. Tingle held certain junior appointments which offered him opportunities for research. Owing, however, to unforeseen family responsibilities he was compelled to give up, for a time, his chosen career of investigation, and taught chemistry in secondary schools.

In 1896 he came to America and was successively professor of chemistry at the Lewis Institute, Chicago (1897–1901), Illinois College, Jacksonville (1901–1904), and assistant in charge of organic chemistry at Johns Hopkins University under Professor Remsen (1904–1907). During his residence in the United States Dr. Tingle became sub-editor and abstractor in organic chemistry on the staff of the *American Chemical Journal*, his work being characterised with care and precision, and as his study of current literature in his chosen field was extensive and exhaustive he spared no pains to make his abstracts clear, complete, and useful. His long training as an abstractor on the staff of the Journal of the Chemical Society specially qualified him to take this important part in organising the organic abstracts for the American journal.

Dr. Tingle was appointed professor of chemistry at McMaster University, Toronto, in 1907, in which post he laboured energetically and faithfully until his death. It was perhaps in teaching, for which he possessed a special talent, that Dr. Tingle did his best

and most valuable work for the country of his adoption. He was insistent on the importance of careful, accurate, and clean crafts-manship, and held that theory was useless and often misleading without a knowledge of how it had been deduced and how it could be applied in practice. He laid special stress on the need of mani-pulative skill of the highest order as a necessary pre-requisite to orderly and clear reasoning and successful results.

Dr. Tingle's original work, embodied in upwards of thirty publi-cations, deals with problems of organic chemistry, and is centred chiefly round the mechanism of the "Claisen reactions" and the products and mechanism of nitration in the benzene series. His last paper, which did not appear in print until after his death, settled certain minor points previously undetermined, and was intended to clear the way for a comprehensive study of the laws governing nitration and the means by which their reactions could be controlled. Dr. Tingle made organic research his life work, and carried through to a successful issue a large number of investigations in his chosen field. He held a first place among organic chemists in Canada, and had he been spared it was expected that he would have been able in a few years to devote himself almost exclusively to research. Much has been lost by his death.

In the sphere of Canadian war work Dr. Tingle was the first to recommend the intensive training of girls for employment in muni-tion and chemical factories in Canada, and laid himself out ener-getically to instruct them towards this end. The extra work involved undoubtedly accelerated his death.

He translated and edited several important works in chemistry. For a long time "Spectrum Analysis," by Landauer and Tingle, was the most comprehensive work on the subject in English.

Dr. Tingle was a kind and generous man, taking a great personal interest in his students and their work and exciting their ambition and enthusiasm for advanced study.

He leaves a widow and two children.

W. R. L.

XXXIV.—*Porphyroxine.*

By Jitendra Nath Rakshit.

The ethereal extract obtained in the estimation of morphine in opium by the process described by the author (*Analyst*, 1918, **42**, 320) left a viscid, brown, crystalline residue on evaporation, which when dissolved in dilute acid always gave a solution, becoming more and more purple on stirring or heating. Previous authors do not agree regarding the composition of this colouring matter; Merck, in 1837, prepared from opium a substance containing its colouring matter, and called it porphyroxine; Hesse remarked (*Annalen,* 1870, **153**, 47) that the substance prepared by the former investigator was a mixture of several alkaloids, one of which is meconidine and another probably rhœadine. The same author (*Annalen, Suppl.*, 1864—1865, **4**, 50) noted that Merck's porphyroxine agrees with rhœadine in method of preparation, properties, and composition. It was thought desirable to investigate whether there is any alkaloid that may be correctly called porphyroxine in Indian opium. The alkaloid now isolated was very likely a constituent of what Dey (*Pharm. J.*, 1882, [iii], **12**, 397) obtained on evaporation of the ethereal extract prepared by shaking an aqueous solution of opium made alkaline with sodium carbonate or ammonia, and apparently also of what Merck called porphyroxine. Considering these facts and that the alkaloid gives a purple solution with dilute acids resembling porphyry, the name porphyroxine may reasonably be retained.

The alkaloid isolated is fairly readily soluble in water, in which respect only it resembles papaverine, codamine, narceine, and codeine, but its other properties are in striking contrast with them; the solutions of the base or its salts are strongly lævorotatory, it does not sublime like codamine, and, unlike codeine, the aqueous solution of its hydrochloride gives a white or pale yellow precipitate with ammonia.

Preparation.—Twenty parts of Indian opium powder and nine parts of freshly slaked lime were triturated in a mortar for five minutes, then 100 parts of water were added gradually during one hour, the trituration being continued. The solution was filtered and the filtrate shaken with an equal bulk of ether for ten minutes in a separator. The ethereal layer was then filtered into another separator containing some dry lumps of calcium chloride, shaken for five minutes, allowed to settle, the ethereal solution decanted, filtered, and evaporated on a water-bath. A pale yellowish-brown,

soft, crystalline residue was obtained, which when rubbed with a spatula on a porcelain plate for three to four hours became a dry powder. One hundred grams of this powder were heated with 200 c.c. of light petroleum until the solvent boiled briskly, the whole was shaken for fifteen minutes, heated again to boiling, and the petroleum decanted as completely as possible, the insoluble residue being carefully excluded. This process of extraction was repeated five times, 100 c.c. of petroleum being used each time, and finally the contents of the flask were collected, dried, and powdered. Ten grams of this powder were triturated with 100 c.c. of 10 per cent. hydrochloric acid gradually added during half an hour, and then with 100 c.c. of water gradually added during another hour, and filtered quickly, the residue being washed with a little dilute hydrochloric acid. To the filtrate was added a saturated solution of sodium hydrogen carbonate, a thin layer of ether being kept on the surface of the liquid, and the latter was stirred until the addition of a further quantity did not produce any effervescence. After remaining for half an hour for the complete separation of the precipitate, this was collected and washed with distilled water. The filtrate, measuring about 500 c.c., was shaken with 50 c.c. of chloroform for fifteen minutes, the chloroform removed, and the process of extraction was similarly repeated thrice with 30, 25, and 25 c.c. of chloroform respectively. The chloroform extracts were mixed together, filtered, the bulk of the solvent was distilled off, and the residue dried slowly on the water-bath; it was then kept overnight in a desiccator. Sometimes the substance formed a soft, viscid, crystalline mass, but generally a pale brownish-yellow, viscid varnish, which on rubbing with a spatula against the side of the basin for an hour became a crystalline, pink powder. Five grams of this powder were heated on a water-bath with 100 c.c. of light petroleum (b. p. 100—120°) just to boiling, the mixture was then shaken for fifteen minutes with a rotatory motion, heated again to boiling, and the petroleum decanted through filter paper, the undissolved residue being carefully excluded. The residue in the flask was again twice extracted similarly with 80 and 60 c.c., respectively, of light petroleum, care being always taken not to melt the substance, thus causing the extraction to be incomplete. The successive petroleum extracts were collected and allowed to evaporate, when the base crystallised in groups of radiating, shining, pale yellow prisms, which were carefully separated from a thin film of non-crystalline residue, powdered, and dried in a desiccator. Several samples from different preparations were analysed, the results of one only being given below:

0·2950 gave 0·7530 CO_2 and 0·1854 H_2O.　C=69·46; H=6·98.

0·253　　,,　　10·6 c.c. N_2 (moist) at 34° and 750 mm.　N=4·36.

$C_{19}H_{23}O_4N$ requires H=6·99; C=69·30; N=4·26 per cent.

Porphyroxine forms pale yellow or white, transparent prisms melting at 134—135° to a clear, transparent, straw-coloured liquid which solidifies on cooling.　It is a non-deliquescent substance appreciably soluble in water, giving a strongly alkaline solution; it is readily soluble in dilute acids, acetone, carbon disulphide, chloroform, or glacial acetic acid, moderately so in benzene, carbon tetrachloride, methyl or ethyl alcohol, toluene, or ethyl acetate, sparingly so in amyl alcohol, ether, light petroleum, ammonia, or barium hydroxide, and almost insoluble in aqueous sodium hydroxide, potassium hydroxide, or lime water.　When its dilute mineral acid solutions are kept exposed to air, they assume a fine pink porphyry colour.　The base has a strongly alkaline reaction towards cochineal, methyl-orange, and litmus, but has no action on phenolphthalein.　Iodine solution gives an orange precipitate with the aqueous solution of the base and a brick-red precipitate with its dilute hydrochloric acid solution.　Mayer's reagent gives a white precipitate with its aqueous solution and the usual pale yellow one with its dilute hydrochloric acid solution.　Colour reactions of the base are often vitiated by the presence of a small quantity of impurity, and the following reactions were observed with a sample specially prepared by recrystallising three times from petroleum. It gives a red colour with concentrated sulphuric acid, a grass-green with concentrated sulphuric acid and a small quantity of potassium dichromate, a pale yellow with concentrated nitric acid, and an orange with concentrated hydrochloric acid; a brownish-red precipitate is obtained on adding ferric chloride to its sulphuric acid solution, and when fused with potassium hydroxide it becomes brown and gives off a strongly alkaline vapour without becoming charred.

0·2540, made up to 50 c.c. with chloroform, gave $\alpha - 4·1°$ (Ventzke) in a 2-dcm. tube at 32°, whence $[\alpha] - 139·9°$.

The *hydrochloride* crystallises from water in prismatic needles. It is a stable salt, and, on heating, softens at 140° and melts at 155° to a clear, pale yellow liquid which does not solidify quickly on cooling:

0·1168 gave 0·0460 AgCl.　Cl=9·7.

$C_{19}H_{23}O_4N,HCl$ requires Cl=9·7 per cent.

It is a non-deliquescent, crystalline, stable substance readily soluble in water, chloroform, methyl or ethyl alcohol, or glacial acetic acid, sparingly so in amyl alcohol or carbon disulphide, and

almost insoluble in acetone, benzene, carbon tetrachloride, ethyl acetate, ether, light petroleum, or toluene.

0·2920, made up to 50 c.c. with water, gave $\alpha - 4·0°$ (Ventzke) in a 2-dcm. tube at 32°, whence $[\alpha] - 118·8°$.

The *platinichloride* separates from a fairly concentrated aqueous solution as a bright, ochreous, crystalline powder.

Found: Pt = 18·0.

$(C_{19}H_{23}O_4N,HCl)_2PtCl_4$ requires Pt = 18·2 per cent.

When kept in a steam-oven for a long time, it slowly swells up and decomposes, forming a dark brown, spongy mass. It darkens at 188° and melts and decomposes at about 204°.

The *aurichloride* was obtained as a greyish-yellow, amorphous precipitate, which decomposed within an hour while remaining in the mother liquor.

The *hydrobromide* crystallises in fine, white needles which melt at 148—150° to a pink liquid:

0·3367 gave 0·1555 AgBr.   Br = 19·7.

$C_{19}H_{23}O_4N,HBr$ requires Br = 19·5 per cent.

It becomes slightly pink after two or three days, and is readily soluble in water, methyl or ethyl alcohol, or glacial acetic acid, sparingly so in acetone, chloroform, or ethyl acetate, and insoluble in amyl alcohol, benzene, carbon disulphide, carbon tetrachloride, ether, light petroleum, or toluene.

0·4209, made up to 50 c.c. with water, gave $\alpha - 4·4°$ (Ventzke) in a 2-dcm. tube at 32°, whence $[\alpha] - 90·6°$.

The *hydriodide* was obtained as a pale brown powder, which melts and decomposes at 115°. The salt, once separated from its aqueous solution, is very sparingly soluble in water, and therefore in the analysis the silver iodide was precipitated from its alcoholic solution:

0·1560 gave 0·8200 AgI.   I = 28·3.

$C_{19}H_{23}O_4N,HI$ requires I = 27·8 per cent.

It is readily soluble in methyl or ethyl alcohols, very sparingly so in water, acetone, chloroform, ethyl acetate, or glacial acetic acid, and insoluble in amyl alcohol, benzene, carbon disulphide, carbon tetrachloride, ether, light petroleum, or toluene.

0·3120, made up to 50 c.c. with alcohol, gave $\alpha - 2·8°$ (Ventzke) in a 2-dcm. tube at 32°, whence $[\alpha] - 77·8°$.

The *sulphate* separated from water in pale pink, radiating plates which, when washed with a mixture of equal parts of absolute alcohol and ether, melted at 193° to a pink liquid, with slight decomposition:

0·5120 gave 0·1794 $BaSO_4$. S = 4·8.

$(C_{19}H_{23}O_4N)_2,H_2SO_4$ requires S = 4·3 per cent.

It is readily soluble in carbon tetrachloride, chloroform, ethyl alcohol, or toluene, and almost insoluble in acetone, amyl alcohol, benzene, carbon disulphide, ethyl acetate, ether, or light petroleum.

0·5600, made up to 50 c.c. with water, gave $\alpha - 7·2°$ (Ventzke) in a 2-dcm. tube at 32°, whence $[\alpha] - 111·4°$.

The *phosphate* did not crystallise from water, but was obtained as a powder, which melted at 117° to a pale brown, transparent liquid :

0·4312 gave 0·1175 $Mg_2P_2O_7$. P = 7·6.

$C_{19}H_{23}O_4N,H_3PO_4$ requires P = 7·3 per cent.

This salt quickly absorbs moisture when left exposed to a damp atmosphere, and becomes viscous. It is readily soluble in water, alcohol, methyl alcohol, or glacial acetic acid, sparingly so in chloroform, ethyl acetate, or ether, and insoluble in acetone, amyl alcohol, benzene, carbon disulphide, carbon tetrachloride, light petroleum, or toluene.

0·5390, made up to 50 c.c. with water, gave $\alpha - 6·1°$ (Ventzke) in a 2-dcm. tube at 32°, whence $[\alpha] - 98·2°$.

The *nitrate* crystallises from water in voluminous, fine, feathery tablets melting at 122° to a transparent, pink liquid. An attempt was made to determine the nitratic nitrogen by the Crum-Frankland method, but as soon as sulphuric acid was mixed with a solution of 0·1367 gram of the nitrate in the nitrometer, a blood-red coloration was at once produced, and only 1·0 c.c. of moist nitric oxide was evolved at 35° and 750 mm. The percentage of nitratic nitrogen thus found is only 0·38, whilst that required for $C_{19}H_{23}O_4N,HNO_3$ is 3·80 per cent. Moreover, duplicate analyses did not always agree, and the nascent nitric acid reacts with the alkaloid before it does with mercury :

0·1965 gave 0·4240 CO_2 and 0·1090 H_2O. C = 58·7 ; H = 6·1.

$C_{19}H_{23}O_4N,HNO_3$ requires C = 58·2 ; H = 6·1 per cent.

It is readily soluble in water, chloroform, methyl or ethyl alcohol, glacial acetic acid, acetone, or carbon disulphide, sparingly so in benzene, carbon tetrachloride, ethyl acetate, ether, or toluene, and insoluble in amyl alcohol or light petroleum.

0·6835, made up to 50 c.c. with water, gave $\alpha - 9·1°$ (Ventzke) in a 2-dcm. tube at 32°, whence $[\alpha] - 115·4°$.

The acetate was obtained as a pale brown, transparent, viscid varnish :

0.2780 gave 0.6610 CO_2 and 0.1920 H_2O.   C = 64.8; H = 7.6.

$C_{19}H_{23}O_4N,C_2H_4O_2$ requires C = 64.8; H = 7.0 per cent.

It is readily soluble in water, chloroform, methyl or ethyl alcohol, or glacial acetic acid, sparingly so in acetone or ethyl acetate, and insoluble in amyl alcohol, benzene, carbon disulphide, carbon tetrachloride, ether, light petroleum, or toluene.

The *oxalate* crystallises from water in long, pale yellow, prismatic crystals, which darken and melt at 182° with effervescence:

0.1670 gave 0.0492 CaC_2O_4. $C_2H_2O_4 = 20.72$.

$C_{19}H_{23}O_4N,C_2H_2O_4$ requires $C_2H_2O_4 = 21.48$ per cent.

It is fairly readily soluble in water, methyl alcohol, or glacial acetic acid, sparingly so in acetone, ether, or ethyl alcohol, and insoluble in amyl alcohol, benzene, carbon disulphide, carbon tetrachloride, chloroform, ethyl acetate, light petroleum, or toluene.

0.9340, made up to 50 c.c. with water, gave $\alpha - 12.3°$ (Ventzke) in a 2-dcm. tube at 32°, whence $[\alpha] - 114.2°$.

The *citrate* is an amorphous, yellowish-white powder, which melts at 82—85° to a transparent, pale brown liquid:

0.1135 gave 0.2680 CO_2 and 0.0735 H_2O.   C = 64.3; H = 7.1.

$(C_{19}H_{23}O_4N)_3C_6H_6O_7$ requires C = 64.1; H = 6.4 per cent.

It is appreciably hygroscopic, readily soluble in water, methyl or ethyl alcohol, or glacial acetic acid, sparingly so in acetone, amyl alcohol, carbon disulphide, chloroform, or ethyl acetate, and insoluble in benzene, carbon tetrachloride, ether, light petroleum, or toluene.

0.1595, made up to 50 c.c. with water, gave $\alpha - 2.0°$ (Ventzke) in a 2-dcm. tube at 32°, whence $[\alpha] - 108.6°$.

The *tartrate* is a pink, crystalline powder, which melts at 116—118° to a pale brown, transparent liquid:

0.1080 gave 0.2475 CO_2 and 0.0650 H_2O.   C = 62.5; H = 6.6.

$(C_{19}H_{23}O_4N)_2C_4H_6O_6$ requires C = 62.4; H = 6.4 per cent.

It is somewhat hygroscopic, readily soluble in water, methyl or ethyl alcohol, or glacial acetic acid, sparingly so in amyl alcohol, benzene, carbon disulphide, chloroform, or ethyl acetate, and insoluble in acetone, carbon tetrachloride, ether, light petroleum, or toluene.

0.1635, made up to 50 c.c. with water, gave $\alpha - 1.8°$ (Ventzke) in a 2-dcm. tube at 32°, whence $[\alpha] - 95.5°$.

The *picrate* is a bright yellow, crystalline powder, which becomes brown at 171° and melts at 198°:

0.1158 gave 0.2258 CO_2 and 0.0510 H_2O.   C = 53.2; H = 4.8.

$C_{19}H_{23}O_4N,C_6H_3O_7N_3$ requires C = 53.7; H = 4.7 per cent.

It is a non-deliquescent, crystalline powder, readily soluble in acetone, chloroform, methyl or ethyl alcohol, glacial acetic acid, or ethyl acetate, sparingly so in water, amyl alcohol, benzene, or carbon disulphide, and almost insoluble in carbon tetrachloride, ether, light petroleum, or toluene.

0·2658, made up to 50 c.c. with water, gave $\alpha - 1·5°$ (Ventzke) in a 2-dcm. tube at 32°, whence $[\alpha] - 49·9°$.

OPIUM FACTORY,
    GAZIPUR, INDIA.

XXXV.—*Coagulation of Metal Sulphide Hydrosols. Part I. Influence of Distance between the Particles of a Sol on its Stability. Anomalous Protective Action of Dissolved Hydrogen Sulphide.*

By Jñanendra Nath Mukherjee and Nagendra Nath Sen.

THE coagulation of the sulphide sols has been studied by a fairly large number of investigators. There is, however, fundamental disagreement between the results obtained by different authors. It was suggested by one of us in a previous paper (*J. Amer. Chem. Soc.*, 1915, **37**, 2024) that the discrepancy is due to the difference in the methods of observation, some of which are undoubtedly defective. The method used in that paper is a comparative one, and is based on visual observation of the changes in the sol with time. It will be conceded that no objection can be taken against it, although it has one disadvantage in so far as it is not instrumental. This does not in any way interfere with the trend of the results. The method is found to be the most suitable one and gives concordant numbers.

Contrary to the observations of Freundlich (*Zeitsch. physikal. Chem.*, 1903, **44**, 129), it was shown that dilution with pure water increases the stability of arsenious sulphide hydrosols to coagulation by electrolytes. The electrolytes studied were all salts of univalent cations. The difficulty in explaining the observed facts on the basis of the adsorption theory as developed by Freundlich (*loc. cit.*; *ibid.*, 1910, **73**, 385; 1913, **83**, 97; **85**, 398, 641) was mentioned. This point has also received attention from Kruyt and Spek. (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **17**, 1158), who examined three electrolytes, namely, the chlorides of potassium,

barium, and aluminium, but could not find the stabilising influence
of dilution of the sols for ions other than potassion. They do not
seem to recognise that the adsorption theory as it stands is in-
sufficient to explain all the facts observed, and do not consider the
influence that the distance between the particles of the sol may
have on the stability of the sol.

Further, Young and Neal (*J. Physical Chem.*, 1917, **21**, 14), in
a thorough study of cupric sulphide hydrosols, remark: "the
amount of electrolyte required is independent of the dilution of
the sol within wide limits. This latter was found to be true within
rather close limits by Freundlich for arsenic sulphide sols." The
method used by Young and Neal consists in mixing equal volumes
(2 c.c. each) of electrolyte and sol and noting the respective con-
centration of electrolyte that just produces complete separation of
the colloid in twenty-four hours and that which just fails to do so.
These two limiting concentrations give a measure of the stability
of the sol or the coagulative power of the electrolyte. This method
is one due to Freundlich, and generally used by other workers. It
will be noted that the concentrations of electrolytes employed are,
necessarily, such as would require a fairly long time for the com-
plete separation of the colloid. In the earlier paper (*loc. cit.*), the
process of coagulation was discussed in detail, and it was stated
that "the time for complete settling is not characteristic of the
rate of coagulation." The justification of any method lies in so
far as it indicates the progress of coalescence. The increased mass
of particles with progress of coalescence introduces a new factor,
namely, their gravitational effect, which masks the true behaviour
of the sol, as will be clear from the following observations on
mercuric sulphide sols.

These sols are opaque unless very dilute. On the addition
of electrolytes, there is a quiescent period followed by a
sharp clearing of the whole liquid. At this stage, the liquid loses
its homogeneous appearance, and visible clots are found suspended
throughout the liquid. As the change is sharp, the times noted by
different observers agree satisfactorily. In this way, it is found
that a mercuric sulphide sol, on saturation with hydrogen sulphide,
requires a longer time for the observed change than when it is not
so treated—the electrolyte concentration, of course, being identical.

These experiments leave no doubt that dissolved hydrogen
sulphide increases the stability of the sol. The subsequent settling
of these clots, however, requires a very long time, which is about
the same for both samples. So long as the respective times required
for the clearing of the sols are very small compared with the time
required for the subsequent settling of the clots, it is found that

the times that are necessary for the complete separation of the colloid do not differ much in the two cases. However, with electrolyte concentrations where the clearing requires intervals comparable with that required for the subsequent settling of the clots, regular differences in stability are observed even if the times necessary for complete separation of the colloid are noted.

Influence of Dilution on the Stability of a Sol.

The method employed is to mix 5 c.c. each of sol and electrolyte in carefully cleansed test-tubes. For reasons discussed in the previous paper, the electrolyte is always added to the sol. Thorough mixing is secured by pouring the mixed liquids from one test-tube to another and repeating the process. The mixed liquid is shaken regularly at short intervals, and the changes with time are observed. As before, the times required for perceptible change in the sol, for the attainment of maximum opacity, and for the first appearance of visible particles are noted. The time for complete separation of the colloid is also noted when thought desirable. The comparison is always carried out side by side. For sols of mercuric and cupric sulphides, the time for the appearance of visible particles is noted. With dilute sols, it is necessary to note the time for complete settling of the particles.

Experiments were made on arsenious sulphide sols with solutions of hydrogen, ammonium, potassium, lithium, barium and aluminium chlorides, aluminium sulphate, and thorium nitrate. With sols of mercuric and cupric sulphides, solutions of potassium, ammonium and barium chlorides, aluminium sulphate, and thorium nitrate only were studied. All the glass vessels were cleansed by dipping them for twenty-four hours in chromic acid solution after they had been washed with dilute alkali hydroxide. The need for scrupulous care in the washing of the vessels and avoiding dust or other impurities cannot be too strongly emphasised. This holds especially for the extremely dilute solutions used in some cases.

(a) *Arsenious Sulphide Sols.*

In the presence of salts having univalent cations, dilution of the sol increases its stability in each case. The magnitude of the stabilising effect of dilution will be evident from table I. The electrolyte concentrations given are *end* concentrations, that is, what results after mixing. Sols mentioned in the several tables are different unless stated otherwise. " Coagulation " means the

breaking up of the colloid into flakes so that the liquid is clear or very slightly coloured.

TABLE I.

Sol A contained 17·58 millimoles of arsenious sulphide per litre. Sol B was prepared by diluting sol A five times, and sol C by diluting sol A ten times, with pure water.

Electrolyte : lithium chloride.

Dilution (after mixing).	Sol. A.	Sol. B.	Sol. C.
$5N/16$ ...	—	—	Coagulation after 20 seconds.
$5N/32$ ...	—	Coagulation after 30 seconds.	Coagulation after 50 minutes.
$N/8$......	Instantaneous coagulation.	Coagulation after half an hour.	Perceptible change after 8 minutes. Coagulation after $2\frac{1}{4}$ hours.
$N/16$ ..	Change perceptible on mixing. Coagulation not observed after $1\frac{1}{2}$ hours.	Change just after mixing not perceptible.	Change perceptible after 45 minutes.

On the other hand, in the presence of the salts of aluminium and thorium, the stability decreases on dilution, as will be seen from table II. The data refer to the same three sols. The observations in tables I and II were completed within two days, and neglecting the slight "ageing" during this interval, the data may be taken as comparable.

TABLE II.

Electrolyte : thorium nitrate.

Dilution.	Sol. A.	Sol. B.	Sol. C.
$N/10,000$	Instantaneous coagulation.	Instantaneous coagulation.	Instantaneous coagulation.
$N/20,000$	Perceptible turbidity just after mixing. Sol changes slowly.	Coagulation in 2 minutes.	Coagulation within half a minute.
$N/30,000$	Perceptible turbidity after half an hour.	Perceptible turbidity after 5 minutes.	Coagulation in 4 minutes.
$N/40,000$	—		Coagulation in 53 minutes.

Solutions of salts of bivalent cations display an interesting aspect of the effect of dilution of the sol on its stability. With dilute

sols, the stability increases on dilution, whereas with sols very rich in sulphide content, the stability diminishes on dilution, and for a rich sol it is possible to reach a limit where on further dilution the sol becomes more stable. Moreover, from table III it will be seen that the stability relations on dilution vary with the concentration of the electrolyte itself.

TABLE III.

Electrolyte: barium chloride.
Arsenious sulphide sol containing 19·45 millimoles per litre.

Dilution of Electrolyte.	Original Sol.	Sol diluted 4 times.	Sol diluted 16 times.
$N/800$ ...	Complete coagulation in 1 minute.	Change perceptible in 20 seconds. Coagulation after 4 minutes.	Perceptible change after 1 minute. Coagulation after 12 minutes.
$N/1000$ ...	Change perceptible after half a minute. Clots appear throughout after 17 minutes.	Change perceptible in 1 minute. Clots appear throughout after 18 minutes.	Change perceptible after 2 minutes. Clots appear throughout after 26 minutes.
$N/1200$ ...	Change perceptible in 2 minutes. Clots appear after 1 hour 7 minutes.	Change perceptible in 2 minutes. Clots appear after 52 minutes.	Change perceptible after about 3 minutes. Clots appear after 1 hour 1 minute.

(b) *Mercuric and Cupric Sulphide Sols.*

In the case of mercuric and cupric sulphide sols, it is found that dilution increases the stability of the sol irrespective of the nature of the electrolyte. The effect cannot reasonably escape observation.

All these apparently anomalous facts can be explained on the assumption that distance between the particles of a sol is an important factor in determining its stability. On the adsorption theory of Freundlich, coagulation is due to the neutralisation of the charge of the particles of the sol by adsorbed cations. Other things being equal, it follows that an increase in the total surface of the colloid would mean a decrease in the surface concentration of the cation, so that a higher concentration of the electrolyte would now be necessary to neutralise the charge on the particles. The amount adsorbed is necessarily small, and its effect can only be perceptible when (a) the difference in surface is great compared with the total quantity of the electrolyte present, that is, (b) when the electrolyte concentration is sufficiently low. It is evident that for the concentrations employed in the case of salts of univalent

cations the difference in stability predicted by the adsorption theory on dilution would be negligible. The adsorption theory thus predicts that dilution of the sol will always diminish its stability, and in the limiting case of salts of univalent cations, this theoretical diminution may not be perceptible.

It has been assumed in the above discussion that the individual particles in the sol do not change in any way on dilution, and hence the total surface of the colloidal particles will decrease proportionally to the dilution of the sol.

The observed increase in stability cannot thus be explained by the adsorption theory as it stands. However, if it is considered that dilution also increases the distance between the particles of a sol, it explains easily the increase in stability observed. It may be stated here that Freundlich's adsorption theory does not contemplate any effect of the distance between colloidal particles on the stability of the sol. The increased distance somehow decreases the facility for coalescence, and thus increases its stability, as will be evident from the sequel.

Dilution thus brings into play two factors which have opposite effects on the stability of the sol. The observed increase or decrease in stability is due to the predominating influence of one over the other. The observations given in table III are instructive. In order that the difference in total surface may have a decisive effect on the stability, the quantities withdrawn by adsorption should be comparable with the total quantity of electrolyte present, that is, appreciable differences in the concentrations of the electrolyte in the bulk of the liquid should result with the different dilutions of the sol employed.

As the dilution of the electrolyte increases, the differences in total surface become more dominant in determining the stability of the sol. On the other hand, if the electrolyte concentration is kept constant, then, as the dilution of the sol increases, the total surface of the colloid decreases rapidly, and the effect of adsorption becomes counterbalanced by that of the increase in distance. This is apparent from table IV.

TABLE IV.

Sol contained 19·45 millimoles of arsenious sulphide per litre. Electrolyte: aluminium sulphate. Dilution, $N/4000$.

Original Sol.	Sol diluted 4 times.	Diluted 16 times.	Diluted 20 times.
Coagulation in 7 minutes.	Coagulates immediately on mixing.	Coagulation in 40 seconds.	Coagulation in 50 seconds.

Further dilutions could not be examined, as it became increasingly difficult to follow the changes in the sol.

With mercuric and cupric sulphide sols, much higher concentrations of electrolytes are required for coagulation, and it is interesting to note that in the case of these sols dilution always increases their stability. This may be ascribed to the fact that these sols are generally poorer in colloid content and that the adsorption is much smaller in comparison with the arsenious sulphide sols used.

It should be remarked that the total surface varies directly with the dilution, whereas the mean distance between the particles varies with the cube root of the dilution.

Comparative Stability of Sols having the same Colloid Content but differing in the Degree of Dispersion.

In the foregoing, it has been assumed that on dilution the individual particles do not suffer any change. The observations of Coward (*Trans. Faraday Soc.*, 1913, **9**, 142) show that dilution does not bring about a proportionate decrease in the number of submicrons, and that the migration velocity of the particles in an electric field changes on dilution. Young and Neal (*loc. cit.*) have also observed an increase in migration velocity on dilution with cupric sulphide sols.

In view of these observations, a comparison of a pair of sols which have the same colloid content, but differ in the degree of dispersion, was thought desirable. This is possible with arsenious sulphide sols. Such a comparison has the advantage that, in reality, two sols are compared, one of which has a smaller number of larger particles, whilst the other has a larger number of smaller particles for the same volume. A simple calculation will show that the mean distance between the particles and the total surface of the colloid in a given volume differ in the same ratio. The ratio is given by $\sqrt[3]{(n_1)} : \sqrt[3]{(n_2)}$, where "$n_1$" and "$n_2$" denote the number of particles present in each case. The relative effects of these factors can thus be compared directly. The finer sol will evidently contain a greater number of particles than the coarser one.

The results leave no doubt as to the greater stabilising effect of increased distance. Of course, here also, with dilute electrolyte solutions and sols differing greatly in the degree of dispersion, the surface effect is perceptible.

By varying the conditions of experiment, a series of sols having the same sulphide content was prepared. For comparison, the coarsest and the finest sols are selected.

TABLE V.

Electrolyte: strontium chloride.

Both sols contained 8·52 millimoles of arsenious sulphide per litre.

Dilution.	Sol I (fine sol).	Sol II (coarse sol).
$N/200$	Coagulation after a few seconds.	Coagulation after a minute.
$N/300$	Coagulation after 2 minutes.	Coagulation after 4 minutes.
$N/400$	Coagulation after 13 minutes.	Turbidity perceptible after 1 minute. A portion of the colloid had separated after 40 minutes.
$N/500$]	The greater portion had separated after 40 minutes.	

It appears that the magnitude of the difference in stability is roughly the same for the different electrolytes. It will be seen from the sequel that dissolved hydrogen sulphide has an anomalous effect on the rate of coagulation of arsenious sulphide sol in the case of certain salts. Here, also, the greater stability of the coarser sol is quite marked. In table VI are given the respective concentrations of an electrolyte which corresponds with about the same coagulation time for these two sols.

TABLE VI.

Comparable concentrations.

Electrolyte.	Sol I.	Sol II.	Remark.
$SrCl_2$	$N/500$	$N/400$	
,, ...	$N/400$	$N/300$	In presence of H_2S.
$LiCl$	$N/8$	$5N/32$	
NH_4Cl	$N/20$	$N/16$	
KCl·	$N/20$	$N/16$	

Influence of Dissolved Hydrogen Sulphide on the Stability of Metal Sulphide Sols.

(a) *Arsenious Sulphide.*

In the paper referred to, it was stated that dissolved hydrogen sulphide stabilises arsenious sulphide sols against coagulation by electrolytes. The electrolytes used at that time were salts of univalent cations. It has subsequently been observed that arsenious sulphide sols behave in an anomalous manner. When solutions of

barium and strontium chlorides, magnesium sulphate, and thorium nitrate are used, the sol containing hydrogen sulphide becomes less stable. Tables VII and VIII show that the diminution in stability is as marked as the increase in stability observed with the other electrolytes. In each set of experiments, the sol and the electrolyte were both saturated with hydrogen sulphide freed from impurities. Five c.c. of each were withdrawn by means of a pipette with the help of a rubber hand pump and kept in separate test-tubes. The liquids were then mixed as usual and kept well corked with india-rubber stoppers. Care should be taken that the liquids do not touch the rubber.

TABLE VII.

Arsenious sulphide sol containing 17·58 millimoles per litre. Electrolyte: aluminium sulphate.

Dilution.	H_2S absent.	H_2S present.
$N/24,000$ ..	Complete coagulation after 2 minutes.	Partial coagulation after $3\frac{1}{2}$ minutes.
$N/30,000$ ..	Partial coagulation after 6 minutes. Complete after 11 minutes.	Only slight turbidity after 21 minutes.

TABLE VIII.

Comparable Concentrations.

	Sol I.		Sol II.		Sol III.	
Electrolyte.	H_2S absent.	H_2S present.	H_2S absent.	H_2S present.	H_2S absent.	H_2S present.
KCl	$N/18$	$N/8$	—	—	$N/16$	$N/8$
NH_4Cl	$N/20$	$N/12$	$N/20$	$N/12$	$N/20$	$N/12$
$BaCl_2$	$N/800$	$N/1000$	$N/800$	$N/1000$	—	—
$SrCl_2$	$N/300$	$N/400$	$N/300$	$N/400$	—	—
$Th(NO_3)_4$	$N/10,000$	$N/12,000$	—	—	—	—

The data with thorium nitrate refer to the sol mentioned in table VII. Sols I and II are the same as those in tables V and VI. Sol III is a fine sol containing 34·8 millimoles of arsenious sulphide per litre.

The results show that the magnitude of the stabilising effect varies somewhat with the quality of the sol used. A quantitative comparison is beyond the scope of the present paper.

(b) *Mercuric Sulphide.*

Hydrogen sulphide has a similar influence on mercuric sulphide sols. Increase in stability was observed for ammonium and

potassium chlorides and a diminution for barium and strontium chlorides.

The sols were prepared as usual from the freshly precipitated hydroxide or sulphide after they had been washed free from electrolytes. The sols had a blackish-grey appearance.

The coagulation of these sols differs in one respect from that of arsenious sulphide sols, possibly due to the fact that they are comparatively poorer in sulphide content. Sols, unless very rich in sulphide, show a minimum coagulation time (as defined here); for example, a mercuric sulphide sol gave a clearance time of about two minutes from $N/20$- to $N/300$-barium chloride. With more dilute solutions, the coagulation time increased rapidly as usual.

(c) *Cupric Sulphide.*

It is well known that dissolved hydrogen sulphide markedly stabilises the pure sulphide sols both in aqueous and non-aqueous media (Lottermoser, *J. pr. Chem.*, 1907, [ii], **75**, 293) and facilitates their solution. It is natural to conclude that the same protective effect would be observed with the sulphides of different metals in the presence of electrolytes. This is, however, not the case here. It has been found that hydrogen sulphide diminishes the stability of cupric sulphide sols. This holds good for all the electrolytes studied, namely, potassium, ammonium, strontium, and barium chlorides, and aluminium sulphate, and the anomaly observed with arsenious and mercuric sulphide sols is absent. Young and Neal (*loc. cit.*) could not find any perceptible effect of hydrogen sulphide on the stability. This is probably due to the method they used.

The observed diminution in stability can be understood from an observation of Young and Neal. They find that hydrogen sulphide diminishes the velocity of migration of the particles of a cupric sulphide sol in an electric field. It follows from the well-known Helmholtz-Lamb formula (*Rep. Brit. Assoc.*, 1887, 495) that a diminution of the electric charge of the particles takes place provided that other factors remain constant. The result will be a diminution in stability, as a smaller amount of adsorbed cations will now be required to discharge the particles. As it is not clear that simultaneous measurements of viscosity and other properties were made, the parallelism loses much of its significance.

Solutions of ammonium, potassium, barium, and strontium chlorides, and aluminium sulphate were studied. With ammonium and potassium chlorides, nearly saturated solutions have to be used.

TABLE IX.

Clearance time.

Electrolyte.	Dilution.	H₂S absent.	H₂S present.
KCl	—	6 minutes.	A few seconds.
BaCl₂	$N/20$	9 ,,	4 minutes.
Al₂(SO₄)₃	$N/2000$	13 ,,	9 ,,

Protective Action of Alkali Sulphides and Alkali Hydroxides.

Solutions of potassium and sodium sulphides have a more marked protective action. This stabilising influence has been found for ammonium, potassium, barium, and strontium chlorides, and aluminium sulphate on hydrosols of cupric, mercuric, and arsenious sulphides. The behaviour of the sols is thus very regular.

This is also the case with alkali hydroxides. A trace greatly facilitates the preparation of sols rich in sulphide, and largely increases their stability. The protective action of alkali sulphides is probably due to the free alkali hydroxide present as a result of hydrolysis.

Since these substances dissolve arsenious sulphide with the formation of arsenites and thioarsenites, it is not possible in this case to refer the protective action observed to the hydroxidions alone. Indeed, the liquid obtained by dissolving in a few c.c. of dilute alkali hydroxide as much arsenious sulphide as possible has an equally marked protective action on the sols of these three sulphides. However, as alkali hydroxide does not react with the other sulphides and produces similar protective action, it is probably that the effect of all these substances is due to the trace of free alkali hydroxide present as the result of hydrolysis.

Freundlich (*Zeitsch. physikal. Chem.*, 1903, **44**, 144) has observed that salts of alkali metals with organic anions of large mass have a lower coagulating power than the corresponding salts of inorganic acids. He refers this to the protective action of these anions, due to greater adsorbability, but in view of the preceding this can as well be due to the trace of alkali hydroxide present on hydrolysis.

In conclusion, it may be stated that the anomalous influence of hydrogen sulphide is not without parallel. Recently Freundlich has found somewhat similar behaviour with ferric hydroxide hydrosol (*Biochem. Zeitsch.*, 1917, **81**, 87). An actual reversion of stability was not, however, observed in this case. So far as can be understood from the abstract of the paper, he explains these irregularities as due to selective adsorption (*loc. cit.*). It remains

to be seen how far these observations can be explained on the basis of the existing theories.

Our best thanks are due to Sir P. C. Rây and to Dr. J. C. Ghosh.

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XXXVI.—*A Simple Form of Apparatus for Estimating the Oxygen Content of Air from the Upper Atmosphere.*

By FRANCIS WILLIAM ASTON.

FROM meteorological considerations, it is probable that air in the stratosphere or isothermal layer is stagnant, hence, owing to their different densities, the relative percentage of oxygen and nitrogen will not be identical with that in the troposphere, where mixing is practically perfect.   It is therefore of great importance that exact analyses should be made whenever possible of samples of air brought down from the great altitudes now available to aeroplanes in order to find out at what height such gravitational separation becomes evident to chemical analysis.   For this purpose, it is enough to determine the oxygen content of the sample after this has been dried and freed from carbon dioxide.

A complete and exceedingly accurate method for determining the percentage of oxygen in air volumetrically has been described by Watson (T., 1911, **99**, 1460).   The apparatus which forms the subject of this paper is a modification of this, in which, by measuring the difference only in oxygen content between the sample and normal air, very considerable simplifications may be made, the pump and the cathetometer being rendered unnecessary.

The samples are contained in test-tubes holding rather more than is required for an analysis (10 c.c.), in the tops of which have been fused a little potassium hydroxide.   Here they remain over mercury for at least two hours before analysis in order to remove carbon dioxide and water vapour.

The measuring burette and barometer tube (see figure) are normally kept full of mercury with the stopcock *A* turned on to avoid fracture by expansion.   In order to perform an analysis, the capillary stopcock *B* is closed and the reservoir *C* lowered until the level of the mercury in the barometer tube is a little below its

upper and broader part. The stopcock A is then closed, and the sample tube held down over the inverted syphon tube in the mercury trough D. When the capillary stopcock B is now opened, the air flows into the upper part of the burette and the mercury rises again to the top of the barometer tube; in order to prevent this happening with destructive violence, the lower part of the barometer is made of capillary bore (less than 2 mm.). After waiting for a few moments for pressure and temperature to adjust
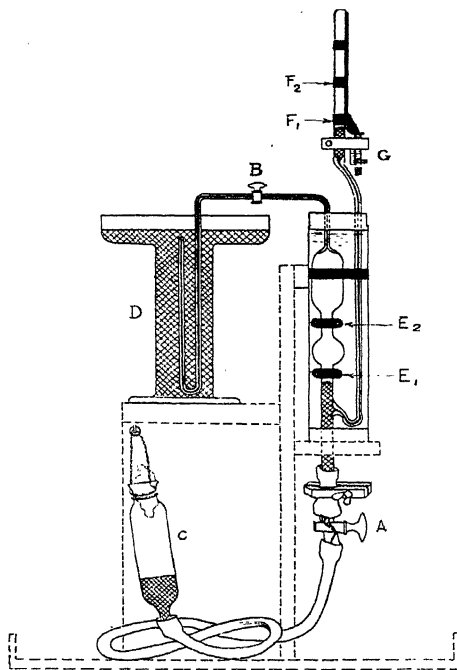
themselves, the sample tube is raised, flooding the end of the inverted syphon with mercury, the stopcock A is opened again, and by lowering the reservoir mercury is caused to flow through the syphon and fill the capillary tube when B is turned off.

It will be seen that the volume of air introduced in this way is constant, being the volume of the upper part of the barometer tube (in the actual apparatus a little less than 10 c.c.); the pressure being atmospheric plus the small difference of level between the

top of the syphon tube and the mercury in the trough, the quantity
will also be approximately constant. This quantity is now accu-
rately measured by adjusting the mercury level in the burette
exactly to the lower fixed reading point, E_1; this can be done with
the greatest nicety by bringing the mercury nearly up to the mark
by manipulation of the reservoir and stopcock, and, finally (with
the latter closed), squeezing the short length of rubber pressure-
tubing with the screw clip provided as indicated. The volumes of
the burette and barometer are such that the surface of the mercury
in the latter will be somewhat as indicated in the diagram, and
the lower movable reading point, F_1, may be exactly adjusted to
it by means of the micrometer screw, G.

The barometer and the parts of the burette where readings are
taken are all made of the same piece of glass tube 0·9 cm. in
internal diameter to eliminate meniscus error. The reading points
are all sleeves of brass tube 1 cm. long fitting the glass tubes,
clamped in the case of the fixed points, sliding loosely in the case
of the moving ones.   ,

The reading of the micrometer having been taken, the air is
now forced into the laboratory tube. This is a quartz test-tube
holding rather more than 10 c.c., to the top of which (not quite
in the centre) has been fused a pellet of phosphorus. These pellets
may be easily made by allowing melted phosphorus to flow from a
pipette with a narrow mouth into a tall cylinder of cold water.
One spherule of about 2—3 mm. in diameter should be ample, and
this is introduced into the inverted quartz tube full of mercury,
shaken into position, and fused into the side with a touch from a
Bunsen flame. When all the air has been transferred from the
burette to the quartz tube, the phosphorus is inflamed and then
heated to boiling point in order to ensure the complete removal of
all oxygen. Some time is allowed for the phosphoric oxide to
settle, when the deoxidised air is drawn back into the burette. It
was feared when the apparatus was designed that to perform this
operation satisfactorily might be difficult, or even impossible, as
small bubbles of air were expected to remain behind on the walls
of the quartz tube, now of necessity contaminated with the pro-
ducts of combustion. Such bubbles are formed, but they can be
dislodged by touching with the syphon tube and then washed with
a little mercury into the burette.   '

In Watson's apparatus, the deoxidised residue was measured at
the same volume as the original air, necessitating the determination
of two widely different pressures. In the present one, the residue
is measured at such a volume that if the air is normal the two
pressures measured would be identical, so that a very small differ-

ence of pressure only need be determined. For this purpose, the upper fixed reading point, E_2, is used, this being set once for all during the construction of the burette, so that the upper part of the burette holds exactly 79·0 per cent. of the whole. The upper movable reading point, F_2, is also soldered to the sliding carrier at exactly the same height above the lower one as that between the fixed points. Hence it will be seen at once that for normal air the mercury at the measurement of the residue should stand at the upper movable reading point, or, if the dimensions of the apparatus are not quite correct, at a constant small distance above or below it, a correction easily determined at any time by an analysis of normal air. If, on the other hand, there is reduction in the percentage of oxygen present, the mercury will stand at a higher level, the difference being measured on the micrometer.

A decrease of oxygen from 21 per cent. to 20 per cent. corresponds with a change in height of mercury in the ratio of 79 to 80; as the normal difference between the fixed and movable reading points in the apparatus in use is 237 mm., this gives exactly 3 mm. per 1 per cent. change. The micrometer has a range of 10 mm., which is more than ample for the changes expected, and analysis should be consistent to well within one-tenth per cent. on total air, the head of the micrometer being divided in twentieths of a millimetre, corresponding with one-sixtieth per cent.

Temperature errors are minimised by the immersion of the burette and the most of the length of the barometer tube in a small water-jacket. As the time occupied in an analysis is only a few minutes, they are not likely to be serious.

The following readings of the micrometer in mm. obtained with the apparatus will serve as an example. The first set of three were obtained with pure air, which is regarded as containing 21·00 per cent. oxygen, the second with an artificial sample in which the oxygen content had been reduced, by the addition of a known quantity of deoxygenated air, to 20·42 per cent. :

	Pure air.			Sample.		
F_1 ...	3·65	3·38	4·83	4·52	5·55	5·40
F_2 ...	3·39	3·20	4·55	6·09	7·21	7·06
Diff.	0·26	0·18	0·28	1·57	1·66	1·54
Mean diff.		0·24			1·59	

Decrease in percentage of oxygen $\frac{1 \cdot 59 + 0 \cdot 24}{-} = 06 \cdot 1$ giving percentage of oxygen in sample $= 20 \cdot 39$, in good agreement with the value expected.

XXXVII.—*The Resolution of Hyoscine and its Components, Tropic Acid and Oscine.*

By HAROLD KING.

HYOSCINE or scopolamine, the tropyl ester of oscine, and one of the group of Solanaceous alkaloids, receives varied and extensive use in medicine, and has on that account attracted the attention of many workers both from the chemical aspect and from the medicinal.

During the last few years, the subject has acquired an additional interest and importance as a result of the recognition that oscine (or scopoline), the basic hydrolytic product, is capable of resolution into its constituents *d*- and *l*-oscine. This follows from the resolution of benzoyloscine by Tutin in 1910 (T., **97**, 1793) and from the partial elucidation of the structural formula of oscine by Schmidt and Hess and their co-workers, whereby it seems certain that oscine, unlike tropine, is not internally compensated. Apart from these two separate results, and in spite of the vast amount of work that has been carried out on oscine and hyoscine, there was nothing known which definitely pointed to this conclusion. Since tropic acid is also capable of resolution, and Gadamer (*Arch. Pharm.*, 1901, **239**, 294) has shown that *l*-tropic acid may be obtained by hydrolysis of *l*-hyoscine, it follows that tropyloscine (hyoscine) might exist in ten, or possibly eleven, stereoisomeric forms consisting of four optically active, four partially racemic, two fully racemic, and one double racemic compound. The problem is in some ways analogous to that presented by the ten tetrahydroquinaldinomethylenecamphors obtained by Pope and Read (T., 1913, **103**, 1515), but with this difference, that in the case of the hyoscines an approach is at present (apart from the rarity of the materials) not possible from the synthetic side, as hyoscine has as yet not been obtained by the esterification of oscine by tropic acid. The elucidation of the chemistry of the isomeric hyoscines and the correct allocation of the medicinal properties to be attributed to each is of considerable moment for both sciences.

Our knowledge of the hyoscines as revealed by previous workers, so far as it appertains to the present subject, may be very briefly summarised.

Naturally occurring *laevo*-hyoscine has been obtained in a state of purity by several workers, and in the form of its well-crystallised hydrobromide is a commercial product. In the plant, it is apparently accompanied to some extent by *dl*-hyoscine, from which

it can be separated by fractional crystallisation of the hydro-bromides. Racemic hyoscine base, which can also be obtained from *l*-hyoscine by the action of alkalis, forms two hydrates, one crystallising with two molecules of water, and known as atroscine (Hesse), the other with one molecule of water. Two attempts to resolve racemic hyoscine are recorded, the first by Schmidt (*Arch. Pharm.*, 1898, **236**, 56), who found that the salt with thiocyanic acid did not separate into two mechanically separable crystalline enantiomorphs, as was the case with racemic lupanine (Schmidt and Davis, *Arch. Pharm.*, 1897, **235**, 196), the second by Gadamer (*Arch. Pharm.*, 1901, **239**, 294), who states that the quinic acid and *d*-mandelic acid salts of *dl*-hyoscine are very readily soluble and possess little crystallising power, and are therefore not suit-able for the resolution of hyoscine.

The primary mode of attack adopted in the present investiga-tion is based on some unpublished preliminary experiments by Tutin, who showed that *l*-hyoscine of commerce forms a soluble, deliquescent salt with *d*-bromocamphorsulphonic acid which can be recrystallised from dry ethyl acetate containing alcohol, and also that when *l*-hyoscine is racemised by alkali, the product as a salt with the same acid can likewise be recrystallised, and the successive fractions of salt so obtained show a progressive variation in rotatory power. The author here gratefully acknowledges his indebtedness to Mr. Tutin for placing these results at his disposal.

A quantity of crystalline hydrobromides of feeble lævorotatory power, obtained as a by-product in the manufacture of the thera-peutically valuable *l*-hyoscine, was fractionally crystallised as a salt with *d*-α-bromo-π-camphorsulphonic acid, when the first salt to be isolated was *meteloidine bromocamphorsulphonate* (m. p. 224—227°). This salt crystallises exceedingly well, and contains *i*-meteloidine (compare Pyman and Reynolds, T., 1908, **93**, 2077). On continuing the fractionation, d-*hyoscine bromo-camphorsulphonate* was obtained in a state of purity. It melted at 159—160°, and crystallised in glistening, acicular needles.

d-*Hyoscine hydrobromide* was prepared from it, and found to crystallise with three molecules of water and to possess a specific rotatory power $[a]_D + 23 \cdot 1°$, which corresponds with a value $[a]_D + 33 \cdot 4°$ for the *d*-hyoscinium ion. For comparison, some of the maximum values recorded by previous observers for the *lævo*-salt are tabulated below.

l-*Hyoscine Hydrobromide.*

	$[a]_b$ anhydrous salt.	$[a]_b$ ionic value.
Schmidt[1]	$-25.7°$	$-32.5°$
Hesse[2]	-25.9	-32.7
Thoms and Wentzel[3]	-25.76	-32.5
Carr and Reynolds[4]	-26.0	-32.8
Willstätter and Hug[5]	-26.0	-32.8
King[6]	-25.9	-32.7

d-*Hyoscine Hydrobromide.*

King[7]	$+26.3°$	$+33.2°$

[1] *Arch. Pharm.*, 1892, **230**, 207.   [2] *J. pr. Chem.*, 1901, [ii], **64**, 353.
[3] *Ber.*, 1901, **34**, 1023.   [4] T., 1910, **97**, 1330.
[5] *Zeitsch. physiol. Chem.*, 1912, **79**, 146.   [6] P. 504.   [7] P. 503.

These values show that the purified l-hyoscine hydrobromide of previous workers and the d-hyoscine hydrobromide now isolated for the first time represent one pair out of the eleven possible stereoisomeric hyoscines.

On mixing equal weights of pure d- and l-hyoscine hydrobromides and recrystallising the mixture from water, dl-hyoscine hydrobromide, also crystallising with three molecules of water and in a form indistinguishable from the active components, was obtained. It differs from the active components in that it very readily effloresces and in that the base obtained from it is crystalline and contains two molecules of water. For the further characterisation of these three related compounds, their *aurichlorides, auribromides,* and *picrates* were prepared. The results are shown in the following table:

	l-Hyoscine.	d-Hyoscine.	dl-Hyoscine.
Base—			
Appearance	Syrup.	Syrup.	Prisms.
H_2O	—	—	$2H_2O$
M. p.	—	—	$38—40°$
Hydrobromide—			
Appearance	Large rhombic tablets.	Large rhombic tablets.	Large rhombic tablets.
H_2O	$3H_2O$	$3H_2O$	$3H_2O$
M. p. (anhydrous)	$193—194°$	$193—194°$	$181—182°$
$[a]_b$ (anhydrous)	$-25.9°$	$+26.3°$	
Picrate—			
Appearance	Slender matted needles.	Slender matted needles.	Needles.
M. p.	$187—188°$	$187—188°$	$173.5—174.5°$

	l-Hyoscine.	*d*-Hyoscine.	*dl*-Hyoscine.
Aurichloride—			
Appearance	Needles, both edges serrated.	Needles, both edges serrated.	Needles, one edge serrated.
M. p.	204—205°	204—205°	214—215°
Auribromide—			
Appearance	Chocolate-red leaflets.		Chocolate-red leaflets.
M. p.	187—188°		209—210°

Some of these call for further remark in view of the results of previous observers. The racemic base crystallising with $2H_2O$ is probably a purer form of Hesse's atroscine (*Ber.*, 1896, **29**, 1776), which melted at 36—37°, and was obtained by fractionally crystallising commercial samples of hyoscine hydrobromide. It was obtained on one other occasion by Gadamer (*Arch. Pharm.*, 1898, **236**, 382), who gives the melting point 37—38°. The *dl*-hyoscine hydrobromide agrees in its properties with those recorded by Hesse (*Annalen*, 1899, **309**, 75; *J. pr. Chem.*, 1901, [ii], **64**, 353).

The picrates have been recommended for identifying the mydriatic alkaloids by Carr and Reynolds (T., 1912, **101**, 949), who describe *l*-hyoscine and *dl*-hyoscine picrates as slender, matted needles melting respectively at 180—181° and 193°. Neither of these melting points is in agreement with the results here recorded, which, however, do find support in the only two other recorded melting points of the picrates: Schmidt (*Arch. Pharm.*, 1894, **232**, 409) describes *l*-hyoscine picrate as melting at 187—188°, and Finnemore and Braithwaite (*Pharm. J.*, 1912, **89**, 136), from an examination of commercial samples of hyoscine hydrobromide of varying rotatory power, give figures which show that *l*-hyoscine picrate melts at 187—188° and *dl*-hyoscine picrate at 174—175°.

The aurichlorides have been described by almost all previous workers on the hyoscines, but there is complete disagreement between the recorded melting points. This is all the more surprising, as several workers have had in hand pure *l*-hyoscine hydrobromide. To quote only two of these, Schmidt (*Arch. Pharm.*, 1910, **248**, 641) states that *l*-hyoscine aurichloride of various origins has previously been shown to melt when quite pure at 210—214°, whereas Hesse (*J. pr. Chem.*, 1901, [ii], **64**, 274) states that after many crystallisations he never found any salt to melt above 198°. The melting points now recorded for the *d*- and *l*-hyoscine aurichlorides are for salts prepared in two different ways and recrystallised to constant melting point. In substantial agreement with these values, Thoms and Wentzel (*Ber.*, 1901, **34**, 1023) give 204°, and Finnemore and Braithwaite (*loc. cit.*) record

several almost pure commercial *l*-hyoscine hydrobromides as furnishing aurichlorides melting at 200—204°.

Tropic Acid. The Acid Constituent of Hyoscine.

As has already been stated, Gadamer showed that *l*-hyoscine on hydrolysis with the base tropine gave *l*-tropic acid. This crude acid, on purification by recrystallisation from water, gave *l*-tropic acid melting at 125—126°, and having a specific rotatory power in water $[\alpha]_D - 71\cdot8°$. Gadamer regarded this as optically pure, since Ladenburg and Hundt (*Ber.*, 1889, **22**, 2591) record the value $[\alpha]_D + 71\cdot4°$ for pure *d*-tropic acid melting at 127—128°.

Instead of employing a base for the hydrolysis, *l*-hyoscine has now been hydrolysed by boiling with dilute hydrochloric acid, when a crude *l*-tropic acid (m. p. 125—127°, $[\alpha]_D - 70\cdot5°$) was obtained, which on recrystallisation gave *l*-tropic acid melting at 127—128° and having $[\alpha]_D - 76°$ in water. As this rotation was numerically considerably greater than the value recorded by the aforementioned workers, it was necessary to repeat the resolution of tropic acid.

A comparison of the results obtained with those of previous investigators is shown in the following table:

	Ladenburg and Hundt.	Amenomiya.[1]	King.
Quinine d-tropate—			
M. p.	186—187°	189—190°	191·5—192·5°
$[\alpha]_D$ 95 per cent. alcohol	—	—	— 114°
Quinine l-tropate—			
M. p.	178°	184—185°	185—186°
$[\alpha_D$ 95 per cent. alcohol	—	—	— 141°
d-Tropic acid—			
M. p.	127—128°	126—127°	128—129°
$[\alpha]_D$ water	—	—	+ 81·6°
$[\alpha]_D$ alcohol	+ 71·4°	+ 71·3°	+ 71·8°
l-Tropic acid—			
M. p.	123°	126°	128—129°
$[\alpha]_D$ water	—	— 72·7°	— 81·2°
$[\alpha]_D$ alcohol ...	— 65·1°	—	—

[1] *Arch. Pharm.*, 1902, **240**, 501.

It is at once seen that Ladenburg and Hundt's value $[\alpha]_D + 71\cdot4°$ is the value in alcoholic solution, Gadamer having regarded it as the value in water, as the aforementioned investigators were not

very explicit, merely stating that the specific rotatory power was $+71\cdot4°$ in solutions of various concentration.

As previous workers appeared to have experienced some difficulty in obtaining pure quinine *l*-tropate from the mother liquors, a variant was made by converting the recovered partly resolved *l*-tropic acid into the quinidine salt. Further, by use of the two stereoisomeric alkaloids quinine and quinidine, but commencing the resolution with quinidine, 55 per cent. of pure quinidine *l*-tropate was first isolated, then an 80 per cent. yield of pure quinine *d*-tropate, and simultaneously a 14 per cent. yield of pure quinine *l*-tropate. On reverting to quinidine, a further 19 per cent. yield of quinidine *l*-tropate was obtained. In this way, approximately 84 per cent. of the tropic acid was resolved into its constituents. It would, however, be probably an advantage, other factors being equal, to start the resolution with quinine and follow with quinidine, since experiment showed that, starting with quinine, 66 per cent. of quinine *d*-tropate was obtained pure, and, as stated above, starting with quinidine only, 55 per cent. of quinidine *l*-tropate could be separated.

It is interesting to note that previous attempts to use quinine and quinidine for the resolution of externally compensated acids, in the above sense, have not always been successful. Whereas Fischer, Scheibler, and Groh (*Ber.*, 1910, **43**, 2022) found that in the resolution of formyl-β-alanine, quinine separated the lævo-component and quinidine the dextro-, Scheibler and Wheeler (*Ber.*, 1911, **44**, 2686) found that in the resolution of *dl*-leucine the same two alkaloids always gave the lævo-acid first. This was also the experience of McKenzie (T., 1899, **75**, 969) in the resolution of mandelic acid.

Oscine.   The Basic Hydrolytic Product of Hyoscine.

There are numerous instances recorded in the literature of the hydrolysis of *l*-hyoscine by alkalis, but the basic hydrolytic product, oscine, $C_8H_{13}O_2N$, was invariably found to be devoid of optical activity, even in the presence of borates or strong acids (Gadamer, *Arch. Pharm.*, 1901, **289**, 322). The only occasion on which *l*-hyoscine has been hydrolysed by acids is recorded by Hesse (*Annalen*, 1892, **271**, 100), who carried out the hydrolysis with concentrated hydrochloric acid in a sealed tube at 80—100°. This furnished the base, oscine, but there is no record of its polarimetric examination.

To decide this matter, pure *l*-hyoscine has now been hydrolysed by boiling with excess of 10 per cent. hydrobromic acid, the change

of rotation being followed polarimetrically. When hydrolysis was complete, the *l*-tropic acid was removed by extraction with ether, and the residual solution of oscine hydrobromide was found to be devoid of optical activity. As Tutin had shown that benzoyl-*d*-oscine on hydrolysis with hydrochloric acid gave *d*-oscine, the hydrolysis of *l*-hyoscine was repeated, using hydrochloric acid. Again the oscine hydrochloride solution was inactive. As it was conceivable that the benzoylation of oscine might have effected some fundamental change in the configuration of oscine, whereby the benzoylated product became externally compensated, and therefore capable of resolution, it was necessary to prove that oscine itself could be resolved into its constituents, *d*- and *l*-oscine.

Several salts of oscine with optically active acids were prepared and examined. The salt with Reychler's camphorsulphonic acid was not obtained crystalline, but with *d*-α-bromo-π-camphorsulphonic acid a markedly crystalline salt was obtained, which melted at 232—233°. This salt, however, proved to be a partial racemate. With *d*-α-bromo-β-camphorsulphonic acid, a very readily soluble, crystalline salt was isolated, but beyond recording a single rotation, it was not followed further, as *d*-tartaric acid was found to be eminently suitable for the resolution of oscine.

The separation of *dl*-oscine into its two pure enantiomorphs can be effected by use of *d*-tartaric acid alone, the acid salts being used for this purpose in aqueous solution. The more sparingly soluble salt, which separated almost pure after two crystallisations, is l-*oscine* d-*hydrogen tartrate monohydrate* (m. p. 173—174°, anhydrous), which crystallises magnificently in clear tablets or octahedra. Employing 14 grams of oscine in combination with a like quantity of *d*-tartaric acid, between 70 and 80 per cent. of this component was separated with no great difficulty. The d-*oscine* d-*hydrogen tartrate* contained in the mother liquors can be obtained pure either by isolation as the *monohydrate*, a very readily soluble, metastable salt melting below 100°, or, preferably, as the stable anhydrous salt (m. p. 167—168°). The proportion of this salt obtained in a state of purity is largely a function of time, as it crystallises very slowly, but uncommonly well, in hexagonal-shaped tablets from the cold, syrupy mother liquors.

l-*Oscine picrate, hydrochloride,* and *base* were obtained without bringing into contact with alkali at any stage, but this was found afterwards to be an unnecessary precaution, as *l*-oscine is not racemised by boiling with 10 per cent. acid or alkali, and only partly by saturated baryta at 150°.

d-*Oscine picrate, hydrochloride,* and *base* were prepared in the usual manner by liberating the base from the hydrogen tartrate

by a strong alkali. The properties of these salts as compared with the *dl*-oscine salts are shown in the following table:

	d-Oscine.	*l*-Oscine.	*dl*-Oscine.
Base—			
Appearance	Needles.	Needles.	Needles or tablets.
M. p.	109—110°	109—110°	109—110°
$[\alpha]_D$ water	+54·8°	−52·4°	—
Picrate—			
Appearance	Dimorphous rhombs and needles.	Dimorphous rhombs and needles.	Flattened rhombs.
M. p.	237—238°	237—238°	237—238°
Hydrochloride—			
Appearance	Warts composed of prisms. Very deliquescent.	Warts composed of prisms. Very deliquescent.	Warts composed of prisms (anhydrous). Tablets (hydrated).
M. p.	273—274°	273—274°	273—274°
$[\alpha]_D$ in water of basic ion	+24·0°	−24·2°	—

It is noteworthy that the active and *dl*-isomerides have the same melting points, and mixtures of the active with the *dl* show no depression of the melting point. In the case of the bases, the melting-point curve is thus of the same type as is found for the camphoroximes.

By hydrolysis of benzoyl-*d*-oscine, Tutin (*loc. cit.*) obtained a value for the *d*-oscinium ion of $[\alpha]_D + 129°$,* which he regarded as only approximate. As this was very different from the value recorded above, it was necessary to repeat the resolution of benzoyl-oscine. Pure benzoyl-*d*-oscine hydrochloride was obtained having a value $[\alpha]_D + 13·4°$ for the benzoyl-*d*-oscinium ion, in agreement with the value $+ 12·9°$ calculated from the rotation of the bromo-camphorsulphonate. This hydrochloride was submitted to hydrolysis by acids and alkalis. In both cases the result was the same, a solution being obtained which, on removal of benzoic acid, gave values $[\alpha]_D + 26·0°$ and $[\alpha]_D + 25·8°$, by acid and alkali hydrolysis respectively, for the *d*-oscinium ion. Moreover, the hydrochloride and picrate were isolated from the product of acid hydrolysis, and the properties were in agreement with the *d*-oscine salts obtained by the tartaric acid resolution of oscine.

Interpretation of Results.

The question now arises, which of the eight possible optically active stereoisomeric hyoscines do *d*- and *l*-hyoscine represent?

* Tutin gives the value $+ 77·7°$, having overlooked the loss of the benzoyl group.

The various possibilities are shown in the following table, the centre column representing optically pure forms, which, combined, as shown by the arrows, yield partially racemic forms :

Partial racemates.	Optically pure forms.	Partial racemates.
	1. *l*-tropyl-*d*-oscine	
5. *dl*-tropyl-*d*-oscine		7. *l*-tropyl-*dl*-oscine
	2. *l*-tropyl-*l*-oscine	
6. *dl*-tropyl-*l*-oscine	3. *d*-tropyl-*d*-oscine	8. *d*-tropyl-*dl*-oscine
	4. *d*-tropyl-*l*-oscine	

Of these, 1 to 6 are at once excluded, since *l*-hyoscine on hydrolysis with acid or alkali gives *l*-tropic acid and *dl*-oscine, whereas benzoyl *d*-oscine under similar conditions yields optically pure *d*-oscine. On these grounds, *l*- and *d*-hyoscine, represented by 7 and 8, are therefore partially racemic esters, *l*-hyoscine being a molecular combination of *l*-tropyl-*d*-oscine and *l*-tropyl-*l*-oscine, whilst *d*-hyoscine is a similar combination of *d*-tropyl-*d*-oscine and *d*-tropyl-*l*-oscine.

The known inactivation of *l*-hyoscine by alkalis would, on this basis, simply consist in the change of configuration of the tropyl portion of the molecule, probably through the intermediary of the

$$\text{CH}_2 \cdot \text{OH} \qquad \text{CH}_2 \cdot \text{OH} \qquad \text{CH}_2 \cdot \text{OH}$$
$$\text{Ph} \cdot \text{C} \cdot \text{CO}_2\text{R} \qquad \text{Ph} \cdot \text{C} : \text{C} {<}^{\text{OH}}_{\text{OR}} \rightleftharpoons \text{Ph} \cdot \text{C} \cdot \text{H}$$
$$\text{H} \qquad \qquad \qquad \qquad \text{CO}_2\text{R}$$
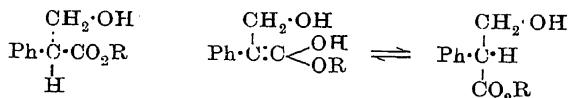
enolic form, and each constituent ester of the partial racemate should give rise to a new ester.

In support of this, some work, which is reserved for future publication, on the re-resolution of racemised *d*-hyoscine has resulted in the isolation of two esters only, *d*- and *l*-hyoscine, which is not surprising, as these, being partial racemates, would contain the four expected optically pure forms.

As opposed to the partial racemic ester nature of *d*- and *l*-hyoscines may be cited the rarity of the occurrence of partial racemates in nature, and the novel behaviour of the hyoscines towards *d*-bromocamphorsulphonic acid, which, so far as *d*-hyoscine is concerned, only resolves *dl* or weakly active hyoscine as far as the partially racemic ester stage. Although this behaviour is, as far as it has been possible to ascertain, unique, it is only necessary to

recall that in the early days of the application of Pasteur's methods of resolution the formation of partially racemic salts was only rarely observed, whereas at the present time it is recognised as of very frequent occurrence.

At the present stage of the investigation there seem to be only two other possible alternatives, both of which appear rather remote. In the first place, *d*- and *l*-hyoscines may be optically pure forms which, owing to some specific effect of the tropyl group, yield *dl*-oscine on hydrolysis, or, secondly, oscine may possess a different configuration in the tropyl ester from that in the benzoyl ester and in the free state, whereby the tropyl group is attached to an internally compensated ψ-oscine, which, on hydrolysis, gives rise to a resolvable oscine.

dl-Hyoscine raises a further difficulty, for there are three possible *dl*-hyoscines, as is shown by the following arrangement:

	Optically pure forms.	Racemates.
	⌠*l*-tropyl-*l*-oscine	
		dl-tropyloscine *A*.
	d-tropyl-*d*-oscine --⟶	
Double racemate *C*.		
	l-tropyl-*d*-oscine	
		dl-tropyloscine *B*.
	--⟶	
	⌊*d*-tropyl-*l*-oscine	

The optically pure forms may be combined in pairs, as indicated, to form two different simple racemates, *A* and *B*, or all four forms may be combined to form a double racemate, *C*. On the acceptation of the partial racemic ester nature of *d*- and *l*-hyoscines, *dl*-hyoscine hydrobromide crystallising with three molecules of water, and obtained by crystallising together equal weights of *d*- and *l*-hyoscine hydrobromides, constitutes a double racemic salt, the absence of any indication of the presence of another salt and the identical crystalline appearance of *d*- or *l*-hyoscine hydrobromide and this salt supporting this view. Moreover, the base crystallising with $2H_2O$ is the base contained in this *dl*-salt, as both give the same picrate.

As has already been indicated in the opening paragraph, there is another hydrate of racemic hyoscine base, containing $1H_2O$ and melting at 56—57°. It was first obtained by Schmidt (*Arch. Pharm.*, 1894, **232**, 409), was re-examined by Luboldt (*ibid.*, 1898, **236**, 11), and more fully investigated by Gadamer (*ibid.*, 382). The last-named investigator showed that the dihydrate can readily

be converted into the monohydrate, but the reverse change was only effected with difficulty. Both hydrates were afterwards described by Hesse (*J. pr. Chem.*, 1901, [ii], **64**, 353), who could not substantiate Gadamer's claims. In reply, Kunz-Krause (*ibid.*, 1901, [ii], **64**, 569) examined Gadamer's three-year-old specimens, and the dihydrate had in every case changed into the base (m. p. 54—55°).

The author has not, so far, been successful in obtaining this monohydrate, so is unable to state with certainty what is the relation between these two racemic hydrates from the point of view of the partial racemic ester nature of *d*- and *l*-hyoscine.

The bearing of these results on the structural formula of oscine deserves a passing notice. The most recent and most complete formula is that put forward by Hess (*Ber.*, 1918, **51**, 1007), who ascribes to oscine the structure

where the linking *a* is regarded as being probably attached to one of the carbon atoms of the piperidine nucleus. The experiments on the stability of the active oscines towards racemising agents certainly support this linking. Pyman and Reynolds (T., 1908, **98**, 2077) have pointed out the close relationship which exists between tropine, oscine, and teloidine, all of which contain eight carbon atoms and a hydroxyl group in the molecule. Moreover, their acyl derivatives are found together in *Datura meteloides*. The author is tempted to make the suggestion that, like tropine, the oxygen atom in question in oscine is attached to the γ-position in the piperidine ring. Oscine would therefore be the internal anhydride of a trihydroxytropine, and this trihydroxytropine may be teloidine. The formulæ suggested are:

Tropine.

d- or *l*-Oscine ?

H- ---OH

H- --H

H--/H

OH

H-/OH-/H

H-

N

Me

Teloidine ?

Teloidine would thus be internally compensated, and in support of this view may be cited the occurrence of meteloidine (tiglyl-teloidine), in nature devoid of optical activity, and the non-resolution of meteloidine by bromocamphorsulphonic acid.   Further, Hess (*loc. cit.*) observed that dihydro-oscine, which undoubtedly has the formula

$$CH_2 \Big\langle {\overset{CH_2—CH——CH·OH}{\underset{CH_2—CH-\ \ -CH·OH}{NMe}}}$$
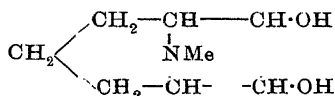
readily produces a silver mirror when treated with ammoniacal silver nitrate solution.   The author finds that teloidine and meteloidine, unlike oscine, also readily reproduce this characteristic of dihydro-oscine, the reducing property being probably associated with the adjacent hydroxyl groups, as is found in tartaric acid.

EXPERIMENTAL.

Resolution of Tropic Acid.

With Quinine.—Following the method described by Ladenburg and Hundt (*Ber.*, 1889, **22**, 2591), tropic acid (25 grams) was neutralised to litmus with quinine base (48·8 grams anhydrous) in hot 50 per cent. alcohol.   A 49 per cent. yield of a quinine tropate separated.   It melted at 176—179°, and had $[\alpha]_D - 126°$ in 95 per cent. alcohol ($c=1$).   For further purification it was recrystallised from 95 per cent. alcohol, and, after five crystallisations, 17 grams of quinine *d*-tropate were obtained pure.   By working once more through the mother liquors, a further 7·4 grams of pure salt were obtained without difficulty.   These two separations combined represent 66 per cent. of the dextro-component.

Quinine *d*-tropate crystallises from 8 parts of boiling alcohol in

groups of radiating needles. In water it is very sparing soluble. It melts at 191·5—192·5° (195·5—196·5° corr.) :

0·1035, dried at 100°, gave 0·2706 CO_2 and 0·0633 H_2O. C=71·3; H=6·8.

$C_{20}H_{24}O_2N_2,C_9H_{10}O_3$ requires C=71·0 ; H=7·0 per cent.

The specific rotation was determined in 95 per cent. alcohol.

$c=1·01$; $l=2$-dcm. ; $\alpha_D - 2°18'$; $[\alpha]_D - 113·8°$.

In absolute alcohol the rotation is smaller.

$c=1·013$; $l=2$-dcm. ; $\alpha_D - 2°6·4'$; $[\alpha]_D - 104·0°$.
$c=1·002$; $l=2$-dcm. ; $\alpha_D - 2°5·4'$; $[\alpha]_D - 104·3°$.

As previous observers appeared to have experienced some difficulty in obtaining quinine *l*-tropate in a state of purity, no attempt was made at this stage to isolate this salt. The mother liquors were therefore combined, and the tropic acid containing excess of the lævo-component was recovered. Small test samples were converted into the neutral salts with brucine, cinchonine, and quinidine, but although the two former gave crystalline salts, the crystallising power of these was not so pronounced as the salt with quinidine. Accordingly, 3·5 grams of this partly resolved tropic acid were crystallised as quinidine salt, when 4·2 grams of quinidine *l*-tropate were obtained of constant specific rotatory power.

Resolution with Quinidine and Quinine.—*dl*-Tropic acid (15 grams) was neutralised with quinidine dissolved in 50 c.c. of 95 per cent. alcohol. On keeping, 22 grams of crystalline material separated. It was obviously a mixture, and had $[\alpha]_D + 151°$ in 95 per cent. alcohol ($c=2$). After four crystallisations, the specific rotation was constant at $[\alpha]_D + 145°$, and the collected quinidine *l*-tropate amounted to 5·5 grams.

Quinidine l-*tropate* crystallises from 95 per cent. alcohol, in which it is soluble in its own weight at 80°, in clusters of well-formed, stout, transparent prisms containing one molecule of water. These exhibit a pronounced heliotrope triboluminescence when powdered in the dark. The air-dried salt when heated in a capillary tube shrinks from about 110°, liquefies between 118° and 120°, and effervesces at 124°. When, however, it is exposed on a watch-glass to a temperature of 90°, it melts completely, and crystallises again on addition of alcohol :

0·2038, air-dried, lost 0·0069 at 100°. $H_2O=3·4$.
0·1029   ,,   gave 0·2590 CO_2 and 0·0672 H_2O.   C=68·7; H=7·3.

$C_{20}H_{24}O_2N_2,C_9H_{10}O_3,H_2O$ requires $H_2O=3·5$; C=68·5 ; H=7·1 per cent.

Its specific rotation was determined in 95 per cent. alcohol, and is dependent on the concentration.

$$c = 0.979 \; ; \quad l = 2\text{-dcm.} \; ; \quad \alpha_D + 2°55\cdot 2' \; ; \quad [\alpha]_D + 149\cdot 1°.$$
$$c = 1.995 \; ; \quad l = 2\text{-dcm.} \; ; \quad \alpha_D + 5°46\cdot 5' \; ; \quad [\alpha]_D + 144\cdot 7°.$$

The mother liquors were worked up further, and gave an additional 7·2 grams, $[\alpha]_D + 146°$. This is approximately a 55 per cent. yield of quinidine l-tropate. As the liquors now showed no tendency to crystallise at all readily, they were combined, and the tropic acid was recovered by use of ether and hydrochloric acid (10 per cent.). On now crystallising as the quinine salt, after three crystallisations, 14·8 grams of quinine d-tropate were obtained pure, $[\alpha]_D - 114°$ ($c = 1$), and a further 2·8 grams with $[\alpha]_D - 1.15°$. The first mother liquors on concentration deposited quinine l-tropate as a homogeneous crop (4·8 grams) of glistening, triangular plates having $[\alpha]_D - 139°$, and melting at 184—185°. It was recrystallised twice from 95 per cent. alcohol, the specific rotation remaining constant at $[\alpha]_D - 140\cdot 7°$ and the melting point at 185—186°, but the form of the crystals changed to needles very similar in appearance to quinine d-tropate.

Quinine l-tropate melts at 185—186° (189—190° corr.). It is very much more readily soluble in hot alcohol than is quinine d-tropate. The diverse crystalline forms described above do not constitute a case of dimorphism, but merely represent extreme crystalline forms. By suitably modifying the conditions of crystallisation, a series of intermediate forms may be obtained consisting of more or less elongated trapezoidal plates. Unlike quinine d-tropate, this salt exhibits a very faint triboluminescence, the intensity of which is not visibly affected by the form of the crystals:

0·1083, dried at 100°, gave 0·2817 CO_2 and 0·0668 H_2O. $C = 71\cdot 0$; $H = 6\cdot 9$.
$C_{20}H_{24}O_2N_2, C_9H_{10}O_3$ requires $C = 71\cdot 0$; $H = 7\cdot 0$ per cent.

The tropic acid contained in the residual liquors was reconverted into the quinidine salt, when 4·3 grams of quinidine l-tropate were obtained, having $[\alpha]_D + 145°$. The residual solution was not further examined.

By the use of the two bases quinidine and quinine, there were thus isolated in an approximate state of purity 88 per cent. of quinine and quinidine l-tropates and 80 per cent. of quinine d-tropate. The proportion of tropic acid resolved is 84 per cent.

Quinidine d-tropate was not isolated, but, on keeping in the ice-chest, a small crop of white, woolly needles separated from the

mother liquors (together with quinidine *l*-tropate), which was probably this salt in an impure condition.

d-*Tropic Acid.*

Pure quinine *d*-tropate (16 grams) was acidified with 50 c.c. of 5 per cent. hydrochloric acid and completely extracted with purified ether. The crude acid so obtained (5·1 grams) melted at 127—128°, and had $[\alpha]_D + 77\cdot2°$ in water ($c=1$). On recrystallisation from water, the melting point rose to 128—129°, and the rotation to $[\alpha]_D + 79°$. After two more crystallisations, the melting point remained unchanged, but the rotation rose to $[\alpha]_D + 81\cdot6°$. The yield was 3·1 grams.

d-Tropic acid crystallises from water in delicate, lustrous scales, which become transformed on keeping in contact with the solution into elongated prisms of hexagonal cross-section. Both forms melt at 128—129° (129—130° corr.) and are anhydrous:

0·2014 was equivalent to 11·9 c.c. $N/10$-baryta.

M.W. = 169. $C_9H_{10}O_3$ requires M.W. = 166.

The specific rotation was determined in alcohol and in water.
In water:

$$c=1\cdot027 \;;\; l=2\text{-dcm.} \;;\; \alpha_D + 1°40\cdot6' \;;\; [\alpha]_D + 81\cdot6°.$$

In absolute alcohol:

$$c=0\cdot997 \;;\; l=2\text{-dcm.} \;;\; \alpha_D + 1°24\cdot2' \;;\; [\alpha]_D + 70\cdot3°.$$
$$c=2\cdot472 \;;\; l=2\text{-dcm.} \;;\; \alpha_D + 3°33\cdot1' \;;\; [\alpha]_D + 71\cdot8°.$$

The specific rotation of the ion was determined by dissolving 0·200 gram of *d*-tropic acid and 0·0638 gram of anhydrous sodium carbonate in water and making up to 20 c.c. The dissolved carbon dioxide was not removed :

$l=2\text{-dcm.} \;;\; \alpha + 1°22\cdot9' \;;\; [\alpha]_D$ for ion $+ 69\cdot4°\;;\; [M]_D$ for ion $+ 114\cdot7°$.
Gadamer (*Arch. Pharm.*, 1901, **239**, 294) has previously noted a fall of rotation of *l*-tropic acid on converting into a salt, but has not followed it quantitatively.

l-*Tropic Acid.*

From Quinidine l-*Tropate.*—Four grams of pure quinidine *l*-tropate, on treatment with hydrochloric acid (10 per cent.) and extraction with ether, gave 1·35 grams of *l*-tropic acid, which, after three crystallisations from water, gave 0·5 gram melting at 128—129° (129—130° corr.). The specific rotatory power was determined in water, and was slightly less than that of the purest *d*-tropic acid :

$$c=0\cdot995 \;;\; l=2\text{-dcm.} \;;\; \alpha_D - 1°37' \;;\; [\alpha]_D - 81\cdot2°.$$

From Quinine l-Tropate.—5·8 Grams of this salt gave 2·0 grams of *l*-tropic acid, which was recrystallised four times from water, giving 1·35 grams melting at 128—129°, and with a specific rotation −81·2°:

$c = 1·002$; $l = 2$-dcm.; $\alpha_D -1°37·6'$; $[\alpha]_D -81·2°$.

l-Tropic acid prepared in this way had the same general properties as the dextro-acid. It is very sparingly soluble in cold benzene, but freely so in cold methyl ethyl ketone or ethyl acetate. From the latter solvent, it crystallises exceedingly well in clear tablets:

0·1975 was equivalent to 11·72 c.c. $N/10$-baryta.

M.W. = 168. $C_9H_{10}O_3$ requires M.W. = 166.

The Resolution of Oscine.

Partial Racemate with d-α-*Bromo-π-camphorsulphonic Acid.*— Two and a-half grams of oscine were converted into this salt, which was very conveniently recrystallised from absolute alcohol. The first crop of crystals weighed 4·9 grams, melted at 232°, and gave $[\alpha]_D +58·8°$ in water ($c = 2$). It was recrystallised twice more from absolute alcohol, yielding, finally, 3·6 grams melting at 232—233°. The specific rotation determined in water was practically unchanged:

$c = 2·001$; $l = 2$-dcm.; $\alpha_D +2°22·4'$; $[\alpha]_D +59·3°$; $[M]_D +276·7°$.

The value for the molecular rotation 276·7° is in good agreement with the molecular ionic value 278·7 for bromocamphorsulphonic acid (Pope and Read, T., 1910, **97**, 2200).

dl-*Oscine* d-α-*bromo-π-camphorsulphonate* crystallises exceedingly well from absolute alcohol in clear, diamond-shaped plates. Ten parts by volume of boiling absolute alcohol are required to dissolve one part by weight of the salt. It melts at 232—233° (237—238° corr.):

0·0995, dried at 100°, gave 0·1703 CO_2 and 0·0526 H_2O.
C = 46·69; H = 5·91.

$C_8H_{13}O_2N,C_{10}H_{15}O_4BrS$ requires C = 46·34; H = 6·05 per cent.

Behaviour with d-α-*Bromo-β-camphorsulphonic Acid.*—Six and a-half grams of oscine were combined with an equivalent of *d*-α-bromo-β-camphorsulphonic acid. The salt could not be obtained crystalline either from water or from a mixture of ethyl acetate and absolute alcohol. A very concentrated solution of the salt in absolute alcohol, however, crystallised as a cake of needles on keeping for a prolonged time in the ice-chest. It was too readily soluble for systematic fractionation from absolute alcohol, and the addition of dry ethyl acetate unexpectedly prevented crystallisa-

tion. The first crop of crystals from absolute alcohol was collected,
and weighed 8·7 grams. It melted at 150—155°, and its specific
rotation was determined in water:

$c = 2·00$; $l = 2$-dcm.; $\alpha_D + 2°27·4'$; $[\alpha]_D + 61·4°$; $[M]_D + 286·3°$.

This product was recrystallised from absolute alcohol, but in
the meantime tartaric acid had effected the resolution of oscine
quite simply, so the investigation of the above salt was dis-
continued.

With Camphor-β-sulphonic Acid.—Attempts to crystallise this
salt were ineffective.

Resolution by d-*Tartaric Acid.*—*dl*-Oscine (13·9 grams) was con-
verted into its *d*-hydrogen tartrate by addition of 13·5 grams of
d-tartaric acid in aqueous solution. The solution was concentrated
to a low bulk, and gave 13·8 grams of a salt crystallising in
hexagonal plates and with a specific rotation $[\alpha]_D + 3·5°$ in water.
After one more crystallisation, it gave 10·2 grams and had
$[\alpha]_D + 1·1°$. This value was not appreciably altered by subsequent
repeated crystallisation, and represents the optical constant of the
salt *l*-oscine *d*-hydrogen tartrate.

l-*Oscine* d-*hydrogen tartrate* crystallises with one molecule of
water of crystallisation in large and clear octahedra. Very often
these have a flattened appearance, and, more rarely, one-half the
faces may be almost entirely suppressed, with the formation of
tetrahedra. Unbroken crystals melt at 134° with effervescence,
but when powdered partly melt at about 130° and gradually
liquefy up to 160°. The anhydrous material melts at 173—174°
(176·5—177·5° corr.). It is readily soluble in cold water, but the
crystals can be washed with 50 per cent. alcohol with little loss.
From dilute alcoholic solutions, this salt tends to separate as an
oil:

0·3126, dried at 105°, lost 0·0181. $H_2O = 5·8$.

$C_8H_{13}O_2N,C_4H_6O_6,H_2O$ requires $H_2O = 5·6$ per cent.

0·1159, dried at 100°, gave 0·1996 CO_2 and 0·0690 H_2O.
$C = 47·0$; $H = 6·7$.

$C_8H_{13}O_2N,C_4H_6O_6$ requires $C = 47·2$ $H = 6·3$ per cent.

The specific rotation was determined in water:

$c = 2·007$; $l = 2$-dcm.; $\alpha_D + 2·56'$; $[\alpha]_D + 1·06°$.

The average value, for nine different samples of the pure salt, of
$[\alpha]_D$ was $+ 1·29°$, the extremes being $+ 0·93°$ and $+ 1·56°$. Taking
this average value for $[\alpha]_D$, the molecular rotation $[M]_D$ is calcu-
lated as $+ 4·18°$, and employing Landolt's value (*Ber.*, 1873, **6**,
1075) for the molecular rotation of ammonium hydrogen tartrate,

$+42.84°$, the value for the l-oscinium ion is $[M]_D -38.66°$, whence $[a]_D -24.7°$.

On continuing the fractionation of the mother liquors, 71 per cent. of the l-oscine d-hydrogen tartrate present was isolated in a state of purity. The separation was materially accelerated by inoculation of the less mobile solutions, followed by addition of alcohol in insufficient amount to precipitate an oil. The residual solutions, now relatively rich in d-oscine d-hydrogen tartrate, were concentrated to a syrup, and, on allowing to remain in a desiccator exposed to a dehydrating agent, crystallised as a striated mass of crystals. These were collected, freed from the adhering syrupy mother liquor, first by suction and then by very limited use of 50 per cent. alcohol as a washing agent. The salt was a mono-hydrate, and gave $[a]_D +23.7°$. It was recrystallised from water, and separated under similar conditions as a felted mass of needles. These now gave $[a]_D + 27.3°$ (anhydrous).

d-*Oscine d-hydrogen tartrate monohydrate* melts from 55° to 65°, forming a meniscus at the latter temperature. It readily effloresces when exposed to the atmosphere, and when dehydrated in a vacuum over sulphuric acid loses its water of crystallisation. The anhydrous material still melts at 55—65°. This is probably the melting point of an amorphous form, as, on keeping, it acquires the melting point of the crystalline anhydrous salt, namely, 163—165° (see below).

Three different samples of the salt were analysed for their water content. The first, representing a freshly collected salt, gave the following result:

0.4502, dried over H_2SO_4, lost 0.0320. $H_2O = 7.1$;

and a salt which showed some signs of efflorescence gave the following:

0.2023 lost 0.0091. $H_2O = 4.5$.

$C_8H_{13}O_2N, C_4H_6O_6, H_2O$ requires $H_2O = 5.6$ per cent.

On keeping for some time, this salt had completely effloresced:
0.1180, dried at 100°, lost nil.
0.1180, dried at 100°, gave 0.2055 CO_2 and 0.0649 H_2O.
$C = 47.5$; $H = 6.15$.

$C_8H_{13}O_2N, C_4H_6O_6$ requires $C = 47.2$; $H = 6.3$ per cent.

The specific rotation of the dehydrated salt was determined in water:

$$c = 0.949 \; ; \; l = 2\text{-dcm.} \; ; \; a_D + 31.1' \; ; \; [a]_D + 27.3°.$$

When the hydrated salt is washed with absolute alcohol, it is transformed into a white, crystalline powder, which is the

anhydrous salt and the stable form at the ordinary temperature. When crystallised from water, the anhydrous salt separates from a syrupy solution very slowly in large, hexagonal-shaped tablets, which, unlike the hydrated salt, can be washed freely with 50 per cent. alcohol. If a syrupy solution is inoculated with a trace of both forms, hydrated and anhydrous, the hydrated form crystallises first, filling the liquid space, and, on keeping, disappears entirely, being replaced by the stable, anhydrous form. For the isolation of pure *d*-oscine *d*-hydrogen tartrate, the latter form is the more convenient. The process is, however, very slow, owing to the solubility of *d*-oscine *d*-hydrogen tartrate and the slow velocity of crystallisation from viscous solutions.

d-*Oscine* d-*hydrogen tartrate* melts at 167—168° (170—171° corr.).

The specific rotation was determined in water and for a salt which had been crystallised to constant rotation:

$c = 1·016$; $l = 2$-dcm.; $\alpha + 34'$; $[\alpha]_D + 27·87°$; $[M]_D + 85·17°$.

This gives a value $+ 42·3°$ for the molecular rotation of the *d*-oscinium ion and $[\alpha] + 27·10°$. This is somewhat greater numerically than the value $[\alpha]_D - 24·7$ obtained by a similar calculation for the *l*-oscinium ion. As this is beyond the limits of experimental error, it is probably another example of the phenomenon first drawn attention to by Pope and Read (T., 1912, **101**, 760), who show conclusively that the molecular rotatory power in aqueous solution of certain salts of the type *l*-base *d*-acid is in agreement with the value calculated from the separate ions, but that the combination *d*-base *d*-acid gives an abnormal value.

l-*Oscine Picrate*.—Six grams of pure *l*-oscine *d*-hydrogen tartrate were added to a boiling saturated solution of 4·25 grams of picric acid in 80 c.c. of water. As the solution cooled, the major portion of the salt crystallised in long needles, but when only luke-warm a denser form appeared in the shape of small, modified rhombs. The yield was 6·35 grams and the melting point 237° (decomp.). The combined product was recrystallised from 35 c.c. of hot water, and, on removing the source of heat, separated at once in long, glistening needles. These were collected while the solution was still warm, the filtrate continuing to deposit solely needles for some time, and then rhombs. The filtrate was heated to dissolve all the crystals, and when cold only deposited the rhomb-like form of crystal, which closely resembles *dl*-oscine picrate. The yield of needles was 4·95 grams, melting at 237—238° (decomp.) (242·5—243·5° corr.), whilst the rhombs amounted to 0·95 gram, and also melted at 237—238° (decomp.). Both forms are

anhydrous, and either form when mixed with *dl*-oscine picrate, which itself also melts at 237—238°, shows no depression of the melting point. At the ordinary temperature, the needle form of picrate is certainly the unstable one, as is readily shown by adding a drop of saturated picric acid solution to a few small crystals of *l*-oscine *d*-hydrogen tartrate and rubbing with a glass rod. The crystals dissolve instantly, and a homogeneous crop of needles first makes its appearance, followed quickly by minute rhombs, and in a short time the needles will have entirely disappeared, their disintegration and solution being readily followed with the aid of a microscope. This behaviour is useful as a test as to whether one is dealing with active or *dl*-oscine salts, since *dl*-oscine picrate has always been observed to separate in small, flattened rhombs.

l-*Oscine Hydrochloride.*—Four grams of *l*-oscine picrate (needle form) were decomposed by shaking with three molecular proportions of 5 per cent. hydrochloric acid, and the picric acid was removed by ether. The solution of the *l*-oscine hydrochloride was completely dehydrated by repeated evaporation to dryness with absolute alcohol, leaving, finally, a white, crystalline powder, which was dissolved in 10 c.c. of boiling absolute alcohol. On keeping, *l*-oscine hydrochloride separated in aggregates of small prisms in the form of warts; a few isolated prisms were also present. The product was collected, and amounted to 1·4 grams. It melted and decomposed at 273—274° (281—282° corr.). A mixture with *dl*-oscine hydrochloride (m. p. 273—274°) also melted at the same temperature. Unlike *dl*-oscine hydrochloride, the *laevo*-salt is very highly deliquescent. A direct comparison of the two was made by exposing a few crystals of each on watch-glasses to the atmosphere. In a few minutes, the *laevo*-salt had completely liquefied, whilst the *dl*-salt was apparently unaffected. On keeping for an hour, however, the latter showed signs of deliquescence, and the deliquesced salt recrystallised in well-formed tablets melting partly at about 100°, and probably representing the monohydrated *dl*-oscine hydrochloride described by Luboldt (*Arch. Pharm.*, 1898, **236**, 18).

The specific rotation of *l*-oscine hydrochloride was determined in water, employing a salt which had been dried at 100°:

$c = 0.997$; $l = 2$-dcm.; $\alpha = -23.6'$; $[\alpha]_D - 19.71°$; $[M]_D - 37.76°$; whence $[\alpha]_D$ for the *l*-oscinium ion is $-24.2°$, whereas the value calculated from the molecular rotation of *l*-oscine *d*-hydrogen tartrate was $-24.7°$.

l-*Oscine Hydrochloride from* l-*Oscine Picrate (Rhombs).*—As has been indicated above, *dl*-oscine picrate and *l*-oscine picrate melt at the same temperature, and the stable modification of

l-oscine picrate crystallises very similarly to *dl*-oscine picrate. It was therefore necessary to prove that this stable form of *l*-oscine picrate did actually contain the active base. Accordingly, 0·5 gram of *l*-oscine picrate (rhombs) was converted as quantitatively as possible by means of ether and three molecular proportions of $N/10$-hydrochloric acid into *l*-oscine hydrochloride. The solution was concentrated somewhat and made up to 20 c.c. In a 2-dcm. tube the observed rotation was $\alpha_D - 25·3'$, from which it is calculated that the *l*-oscinium ion has $[\alpha]_D - 21°$, a value in good agreement with that observed directly for *l*-oscinium hydrochloride. The solution was then dried, and the hydrochloride recrystallised from alcohol. It gave 0·11 gram of highly deliquescent *l*-oscine hydrochloride melting at 271—272°, and when tested with saturated picric acid solution gave the unstable needle form of *l*-oscine picrate, changing into rhombs.

l-*Oscine Base*.—To avoid the action of alkalis, which it was thought might cause partial racemisation, *l*-oscine base was prepared as follows. *l*-Oscine picrate (4·75 grams) was treated with three equivalents of dilute sulphuric acid solution, and the picric acid removed by purified ether. After treating with charcoal to remove the last traces of picric acid, the solution was concentrated under diminished pressure to about 20 c.c., and excess of pure barium carbonate added. On allowing to remain overnight, the solution was free from sulphanion, and only contained *l*-oscine partly present as carbonate. The major portion of the *l*-oscine was readily removed by extraction with freshly purified chloroform, the remainder being retained by the dissolved carbon dioxide. When the latter solution was evaporated to dryness in a vacuum over sulphuric acid and redissolved in a little water, the rest of the oscine was readily extracted by chloroform. In this way, the *l*-oscine was recovered quantitatively as base. The first chloroform extract on complete removal of the solvent crystallised at once. The product was white and amounted to 1·45 grams. It had a specific rotatory power of $[\alpha]_D - 52·8°$ in water. It melted at 109—110°, the same as *dl*-oscine, whilst a mixture of the two showed no depression of the melting point. When recrystallised from light petroleum, it separated in long needles. The melting point was unchanged at 109·5—110·5° (corr.).

The specific rotatory power was determined in water:

$$c = 1·010; \quad l = 2\text{-dcm.}; \quad \alpha - 1°3·6'; \quad [\alpha]_D - 52·4°.$$

With Mayer's reagent (potassium mercuric iodide), *l*-oscine base gives no precipitate, but in the form of a salt it gives a crystal-

line precipitate. The presence of a slight excess·of acid prevents the separation of crystals. *dl*-Oscine behaves similarly.

Action of Acids and Alkalis on l-*Oscine.*—A solution of 0·2 gram of *l*-oscine in water having an observed rotation of $\alpha_D -1°1·7'$ in a 2-dcm. tube was treated with one drop (0·04 c.c.) of 50 per cent. potassium hydroxide solution. After nineteen hours, the observed rotation was unchanged, $\alpha_D - 1°1·5'$.

The same solution was heated on the boiling-water bath for an hour. At the end of this period, the rotation was still $-1°1·7'$. Five c.c. of 50 per cent. potassium hydroxide were now added, and the solution was boiled for an hour. Making a correction for the change in volume, the observed rotation was unchanged, $\alpha_D - 1°1·2'$. This means that 0·2 gram of *l*-oscine was not racemised by boiling for an hour with excess of 10 per cent. potassium hydroxide solution.

There was, however, partial racemisation when 0·2 gram of *l*-oscine was heated with 15 c.c. of saturated baryta solution for four hours at 150°, the value of $[\alpha]_D$ having fallen to about one-half its original value.

The action of boiling 10 per cent. hydrobromic acid also failed to racemise *l*-oscine, for 1 gram of *l*-oscine *d*-hydrogen tartrate in 30 c.c. of 10 per cent. hydrobromic acid had an observed rotation, $\alpha_D -21·1'$, in a 2-dcm. tube, and after three hours' boiling the rotation was practically unaltered, $\alpha_D - 22·6'$.

d-*Oscine Base.*—One gram of pure *d*-oscine *d*-hydrogen tartrate was dissolved in 10 c.c. of 5 per cent. sodium hydroxide solution, and the base extracted with purified chloroform. The combined extracts were clarified by shaking with anhydrous potassium carbonate, filtered, and the solvent removed by distillation. The residual base crystallised instantaneously throughout on touching one spot with a glass rod. A similar very high velocity of crystallisation had previously been noticed with the chloroform-free *laevo*-oscine base. It was crystallised from light petroleum, and separated in long, radiating needles, often forming fasciated growths. It melted at 109—110° (109·5—110·5° corr.), and a mixture with pure *dl*-oscine also at the same temperature.

Its specific rotation was determined in water:

$$c = 1·029; \quad l = 2\text{-dcm.}; \quad \alpha_D + 1°7·6'; \quad [\alpha]_D + 54·8°.$$

d-*Oscine Picrate.*—The solution of the base which had been used for determining the rotatory power was treated with an equivalent of picric acid (0·3 gram) and rapidly concentrated to about 10 c.c. On allowing to cool, long, radiating, glistening needles of *d*-oscine

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picrate (0·3 gram) separated. These melted at 237—238°
(242·5—243·5° corr.). The mother liquors were concentrated,
and, when quite cold, the stable dimorph separated in small,
flattened rhombs exactly as observed in the case of *l*-oscine picrate.
This form also melted at 237—238°. A mixture with *d*-oscine
picrate, obtained by acid hydrolysis of benzoyl-*d*-oscine, also melted
at the same temperature.

d-*Oscine Hydrochloride.*—To complete the analogy with the
laevo-series, this salt was prepared and its specific rotation deter-
mined. For this purpose, 0·2078 gram of *l*-oscine base was
neutralised with the calculated quantity, 13·4 c.c., of $N/10$-hydro-
chloric acid, and the volume made up to 20 c.c. In a 2-dcm. tube
was found α_D 30·1′, whence $[\alpha]_D$ for the *d*-oscinium ion is $+24·0°$,
a value in agreement with $[\alpha]_D - 24·2°$ observed for the *l*-oscinium
ion.

The solution just employed was evaporated to dryness and the
residue crystallised from absolute alcohol, when *d*-oscine hydro-
chloride separated in warts with a few isolated prisms. The melt-
ing point was 273—274°, and the salt was very deliquescent.

Resolution of Benzoyloscine.

This was effected substantially as described by Tutin (T., 1910,
97, 1793).

Five grams of *dl*-oscine hydrobromide were converted into the
base, which was heated to 160° with 10 c.c. of benzoyl chloride,
when a brisk reaction ensued with simultaneous crystallisation of
the benzoyloscine hydrochloride. The solid was collected, washed
with ether, and dried at 100°. The crude product melted at 240°
and amounted to 5·45 grams, that is, an 83 per cent. yield. It
was dissolved in water, and the solution, after decolorisation with
a little charcoal, was rendered alkaline with sodium hydrogen
carbonate, and completely extracted with chloroform. The
benzoyloscine left on removing the chloroform was neutralised to
litmus with *d*-α-bromo-π-camphorsulphonic acid, and the salt frac-
tionated from absolute alcohol. The *d*-benzoyloscine bromo-
camphorsulphonate was obtained pure after three crystallisations,
and melted at 247—248° (Tutin gives 246—246·5°). The specific
rotation was determined in water:

$c = 1·998$; $l = 2$-dcm.; $\alpha_D + 2°11·3′$; $[\alpha]_D + 54·74°$; $[M]_D + 312·3°$.
The calculated value of the molecular rotatory power of the
d-benzoyloscinium ion is therefore $312·3 - 278·7 = 33·6°$, whence
$[\alpha]_D$ for the *d*-benzoyloscinium ion is $+12·9°$.

Benzoyl-d-*oscine Hydrochloride.*

Pure benzoyl-*d*-oscine bromocamphorsulphonate (2·8 grams) was triturated with 30 c.c. of water and three molecular proportions of sodium hydrogen carbonate. Benzoyl-*d*-oscine base appeared to separate in needles, which were immediately dissolved by chloroform. The free base, on removal of the solvent, was exactly neutralised with $N/10$-hydrochloric acid, and, after filtering from a little greasy matter, was concentrated rapidly under diminished pressure to a very small volume. On keeping for a short time, the whole of the liquid became filled with perfectly formed rectangular leaflets, which in a few hours were completely transformed into fine needles. These were collected and washed with absolute alcohol. They amounted to 1·1 grams, and melted and decomposed at 280° (287° corr.) (Tutin gives 283—284°). The product was anhydrous. Its specific rotation was determined in dilute aqueous solution:

$c = 2·005$; $l = 2$-dcm.; $\alpha_D + 28·35'$; $[\alpha]_D + 11·79°$; $[M]_D + 34·83°$.

From this is calculated $[\alpha]_D + 13·4°$ for the benzoyl-*d*-oscinium ion, a value which compares favourably with the value $+ 12·9°$ calculated above from the bromocamphorsulphonate. This value is somewhat higher than Tutin's value, $[\alpha]_D + 10·0°$, which is obtained by calculation from the value $[M]_D + 297·0°$ for benzoyl-*d*-oscine bromocamphorsulphonate.

Hydrolysis of Benzoyl-d-*oscine.*

With Hydrochloric Acid.—The solution just employed (20 c.c.), containing 0·4001 gram of benzoyl-*d*-oscine hydrochloride, was treated with 9·7 c.c. of 31 per cent. hydrochloric acid, thus bringing the volume approximately to 30 c.c. and the strength of the acid to 10 per cent. The rotation was observed, and the solution was then boiled gently to hydrolyse the benzoyl-*d*-oscine, the rotation being observed at intervals, just as is described under the hydrolysis of *l*-hyoscine (p. 507).

Initial reading, $+ 20'$; $l = 2$-dcm.
After 1 hour's boiling, $+ 20·5'$.
After 3 hours' boiling, $+ 22·0'$.

Hydrolysis was now complete, as there was a copious separation of benzoic acid, and the solution gave no turbidity with Mayer's reagent. The observed rotation is therefore due to the *d*-oscinium ion, and the final value, $+ 22'$, corresponds with a specific rotation of the *d*-oscinium ion of $+ 26°$, which is of the same order as that

obtained by calculation from the rotation of d-oscine d-hydrogen tartrate, namely, $[\alpha]_D$ 27·1°, and that directly observed, $[\alpha]_D$ 24·0°, for d-oscinium hydrochloride prepared from the tartrate.

The free benzoic acid was removed by extraction with purified ether, and the aqueous liquor concentrated to a syrup under diminished pressure on the water-bath. On dehydration of the syrup by evaporation with absolute alcohol, the residue crystallised. It was dissolved in a little hot absolute alcohol, and, on keeping, 0·07 gram of crystals resembling ammonium chloride were collected. They melted and decomposed in the neighbourhood of 243° (pure d-oscine hydrochloride melts at 273°), and were highly deliquescent.

Twenty milligrams of this salt, when treated with an equal weight of picric acid in hot aqueous solution, gave a picrate crystallising in long, fine needles, and later a few rhombs separated, a behaviour which is exactly reproduced by the addition of picric acid solution to the pure d- or l-oscine d-hydrogen tartrates (p. 495). This picrate, when collected and dried, melted and decomposed at 237—238°. A mixture with d-oscine picrate melted in the same bath at 237—238°. The alcoholic mother liquors of the above 0·07 gram of d-oscine hydrochloride were combined with picric acid (both in aqueous solution). The addition of the picric acid first precipitated amorphous matter, which was separated, and later a well-crystallised picrate. This salt crystallised in small rhombs, melted and decomposed at 235°, and was in all probability the stable form of d-oscine picrate.

With Alkali.—Pure benzoyl-d-oscine hydrochloride (0·4009 gram) was dissolved in water, and 5 c.c. of 10 per cent. sodium hydroxide were added. The oily base, which separated rapidly, disappeared on boiling. After an hour, the solution was cooled and neutralised to Congo paper with hydrochloric acid. The precipitated benzoic acid was completely removed by ether extraction, and the extracted aqueous liquor was also free from non-hydrolysed benzoyloscine, as was indicated by the absence of a turbidity on treatment with Mayer's reagent in acid solution. In neutral or very faintly acid solution it gave the well-crystallised precipitate observed with oscine salts. The solution was rapidly concentrated and made up to 20 c.c. In a 2-dcm. tube it gave α_D +32·8′, whence the d-oscinium ion has $[\alpha]_D$ +25·8°, a value in good agreement with that observed by acid hydrolysis, $[\alpha]_D$ +26·0°, and that observed for pure d-oscine hydrochloride, $[\alpha]_D$ +24·0°.

d-*Hyoscine.*

The starting material for the isolation of *d*-hyoscine consisted of 75 grams of well-crystallised hydrobromides obtained as a by-product in the manufacture of *l*-hyoscine. It was slightly lævo-rotatory, having $[\alpha]_D - 4\cdot1°$ ($c = 2\cdot3$, anhydrous), and contained 9 per cent. of water of crystallisation, which was lost over sulphuric acid. It was regenerated to base, using sodium hydrogen carbonate and chloroform for the purpose, the weight of base being about 55 grams. This was converted into its salt with *d*-α-bromo-π-camphorsulphonic acid, and crystallised from a mixture of dry ethyl acetate and absolute alcohol. In a few days there was a copious, crystalline separation, which was collected, and amounted to 38·5 grams. It was deliquescent and had $[\alpha]_D + 46\cdot4°$ ($c = 2$), and on two more crystallisations gave 8·8 grams of pure meteloidine bromocamphorsulphonate.

Meteloidine d-α-*bromo-π-camphorsulphonate* crystallises exceedingly well from absolute alcohol, in which it is soluble to the extent of about 1 part in 10 (boiling), or from a mixture with dry ethyl acetate in clusters of prisms. It also crystallises well from water. It melts at 224—227° (228·5—231·5° corr.), and is anhydrous:

0·1410 gave 0·2547 CO_2 and 0·0808 H_2O. C = 49·3; H = 6·4.
$C_{13}H_{21}O_4N, C_{10}H_{15}O_4BrS$ requires C = 48·75; H = 6·4 per cent.

Its specific rotatory power was determined in water:

$c = 2\cdot039$; $l = 2$-dcm.; $\alpha_D + 1°56'$; $[\alpha]_D + 47\cdot42°$; $[M]_D + 268\cdot7°$.

This value for the molecular rotation is somewhat smaller than that given by Pope and Read for the bromocamphorsulphonic acid ion (T., 1910, **97**, 2200). That the meteloidine was inactive was confirmed in two ways:

(1) A small quantity of the above salt was converted into base, avoiding conditions which might favour racemisation by using sodium hydrogen carbonate and chloroform. The base crystallised readily, and was identical in appearance and other properties with a sample of meteloidine kindly supplied by Dr. Pyman, and which was known to be inactive (Pyman and Reynolds, T., 1908, **93**, 2077).

(2) One-half a gram of *i*-meteloidine base was converted into its bromocamphorsulphonate, and the solution evaporated to dryness with absolute alcohol. The crystalline residue was triturated with a little dry ethyl acetate, in which the crystals are practically insoluble, and collected. The rotation of this salt, representing

practically the whole of the meteloidine, was found to be the same as the previously described salt:

$c = 1.969$; $l = 2$-dcm.; $\alpha + 1°51'$; $[\alpha]_D + 47.0°$; $[M]_D + 266.3°$.

It melted at 224—225°, and a mixture of the two salts showed no depression of the melting point.

Isolation of d-*Hyoscine Bromocamphorsulphonate.*—On continuing the fractionation, the original mother liquors gave a second crop of crystals, 24.5 grams, $[\alpha]_D + 44.5°$, which, after ten recrystallisations, gave 11.6 grams of pure d-hyoscine bromocamphorsulphonate melting at 159—160° and having $[\alpha]_D + 60.1°$. This was twice more recrystallised, and gave 8.3 grams with $[\alpha]_D + 60.3°$.

d-*Hyoscine* d-α-*bromo-π-camphorsulphonate* crystallises from a mixture of absolute alcohol and excess of dry ethyl acetate in clusters of glistening, acicular needles. After being dried at 110° it melts at 158—160° (161.5—163.5° corr.). Its specific rotation was determined in water at 16°.

$c = 2.005$; $l = 2$-dcm.; $\alpha + 2°25'$; $[\alpha]_D + 60.3°$; $[M]_D + 370.5°$.

From this it is calculated that the molecular rotatory power of the d-hyoscinium ion is 91.8° and the specific rotatory power $[\alpha]_D$ is $+ 30.2°$ (see d-hyoscine hydrobromide). The salt is not deliquescent:

0.2730 lost 0.0022 at 100°. Loss = 0.8.

0.1238, dried at 100°, gave 0.2394 CO_2 and 0.0675 H_2O. C = 52.8; H = 6.1.

$C_{17}H_{21}O_4N, C_{10}H_{15}O_4BrS$ requires C = 52.7; H = 5.9 per cent.

The fractionation of the various liquors was continued, when further small quantities, 4.5 grams in all, of meteloidine bromocamphorsulphonate, and an additional 12.5 grams of pure d-hyoscine bromocamphorsulphonate, $[\alpha]_D + 60.5°$, were obtained. The original mother liquors now gave 10 grams of a deliquescent salt, $[\alpha]_D + 30.8°$, and 2.7 grams, $[\alpha]_D + 27.3°$, both of which had the properties of a slightly impure l-hyoscine bromocamphorsulphonate, which requires a calculated value of $[\alpha]_D + 29°$. On recrystallisation, these gave salts of higher specific rotation. It was not found possible to isolate pure l-hyoscine bromocamphorsulphonate from the mother liquors.

d-*Hyoscine Hydrobromide.*—Six grams of pure d-hyoscine bromocamphorsulphonate were converted into base, using chloroform and sodium hydrogen carbonate for the regeneration. The base was neutralised with hydrobromic acid and the solution concentrated under diminished pressure. d-Hyoscine hydrobromide separated on keeping in large tablets (2 × 1 cm.).

d-*Hyoscine hydrobromide* crystallises exceedingly well from water in rectangular-shaped tablets with bevelled edges. It crystallises with three molecules of water, the hydrate melting in a capillary tube at $54 \cdot 5$—$55°$ ($54 \cdot 5$—$55°$ corr.). It is rendered anhydrous by drying over sulphuric acid in a vacuum. The behaviour of the anhydrous salt on heating is very varied. It sometimes melts sharply at $168°$, resolidifies, and melts at 193—$194°$ (197—$198°$ corr.). Occasionally, the intermediate melting point is not observed at all, or is only indicated by a slight shrinking. If the anhydrous salt is dried for half an hour at $120°$, only the higher melting point, 193—$194°$, is observed. The probable explanation is that the product, which melts at $168°$, is either an amorphous form or a metastable, crystalline form of the anhydrous salt, and the transformation of one form into the other is accelerated by rise of temperature. *l*-Hyoscine hydrobromide behaves similarly :

$0 \cdot 1842$, dried over H_2SO_4, lost $0 \cdot 0228$. $H_2O = 12 \cdot 38$.

$0 \cdot 1813$, dried at $100°$, lost $0 \cdot 0226$. $H_2O = 12 \cdot 47$.

$0 \cdot 1587$,   ,, $100°$ gave $0 \cdot 0778$ AgBr.   Br = $20 \cdot 85$.

$C_{17}H_{21}O_4N,HBr,3H_2O$ requires $H_2O = 12 \cdot 33$ per cent.

$C_{17}H_{21}O_4N,HBr$ requires Br = $20 \cdot 80$ per cent.

The specific rotatory power of the hydrated salt was determined in water :

$$c = 2 \cdot 842 \, ; \; l = 2\text{-dcm.} \, ; \; \alpha + 1°18 \cdot 5' \, ; \; [\alpha]_D + 23 \cdot 02°.$$
$$c = 2 \cdot 525 \, ; \; l = 2\text{-dcm.} \, ; \; \alpha + 1°10' \, ; \; [\alpha]_D + 23 \cdot 10°.$$

The mean of these values gives for the anhydrous salt $[\alpha]_D + 26 \cdot 3°$ and for the *d*-hyoscinium ion $[\alpha]_D + 33 \cdot 2°$. The latter value is in approximate agreement with that calculated from the molecular rotation of the bromocamphorsulphonate (p. 502), namely, $+ 30 \cdot 2°$.

d-*Hyoscine Aurichloride.*—*d*-Hyoscine bromocamphorsulphonate ($0 \cdot 3$ gram) was dissolved in 5 c.c. of warm water, and 5 c.c. of 10 per cent. hydrochloric acid were added, followed by 7 c.c. of gold chloride solution (1 in 30). The aurichloride separated, partly in isolated, minute, rectangular plates, but for the most part in fern-like growths or spangles. It melted at 202—$203°$ and weighed $0 \cdot 32$ gram. It was twice recrystallised from $2 \cdot 5$ per cent. hydrochloric acid, the melting point each time remaining at 204—$205°$ (208—$209°$ corr.) (decomp.). The recrystallised solid separated in long, flattened, orange-yellow needles with both edges serrated :

$0 \cdot 1266$, air-dried, gave $0 \cdot 0387$ Au.   Au = $30 \cdot 6$.

$C_{17}H_{21}O_4N,AuCl_3,HCl$ requires Au = $30 \cdot 7$ per cent.

d-*Hyoscine Picrate*.—Prepared from *d*-hyoscine bromocamphorsulphonate by double decomposition in aqueous solution, this salt separated as a netted mass of needles melting and decomposing at 187—188° (see *l*-hyoscine picrate).

l-Hyoscine.

l-Hyoscine Hydrobromide.—The properties of this salt are the same as those of *d*-hyoscine hydrobromide. The rotation of the purest hydrobromide crystallised from water was a fraction less than *d*-hyoscine hydrobromide. For various samples, the following values were obtained:

$$c = 2 \cdot 454 \; ; \; l = 2\text{-dcm.} \; ; \; a = -1°7' : \quad [a]_D - 22 \cdot 75°.$$
$$c = 2 \cdot 543 \; ; \; l = 2\text{-dcm.} \; ; \; a = -1°9 \cdot 3' ; \quad [a]_D - 22 \cdot 71°.$$
$$c = 2 \cdot 045 \; ; \; l = 2\text{-dcm.} \; ; \; a = -55 \cdot 43' ; \quad [a]_D - 22 \cdot 58°.$$

The mean of the first two values gives $[a]_D - 25 \cdot 93°$ for the anhydrous salt, and for the *l*-hyoscinium ion $[a]_D - 32 \cdot 73°$, whereas for the purest *d*-hyoscine hydrobromide the values were 26·3° and 33·2° respectively. The use of *l*-α-bromo-π-camphorsulphonic acid for purifying the *l*-hyoscine would no doubt lead to complete accord between the rotatory powers of the two enantiomorphs.

l-Hyoscine Aurichloride.—*l*-Hyoscine hydrobromide (0·2 gram) was converted into base, using sodium hydrogen carbonate and chloroform. A solution of the hydrochloride was mixed with gold chloride solution, and the *l*-hyoscine aurichloride collected. It weighed 0·28 gram, and melted and decomposed at 204—205°. It was recrystallised from one hundred times its weight of 2·5 per cent. hydrochloric acid, and separated in complex, needle-shaped growths serrated on both edges, exactly as observed for the dextro-enantiomorph. The melting and decomposing point was unchanged (208—209° corr.):

0·1075, air-dried, gave 0·0331 Au.   Au = 30·8.

$C_{17}H_{21}O_4N, AuCl_3, HCl$ requires Au = 30·7 per cent.

l-Hyoscine Auribromide.—This was prepared by Jowett's method (T., 1897, **71**, 680), by dissolving 0·2 gram of *l*-hyoscine hydrobromide in excess of hydrobromic acid and adding gold chloride solution. The yield was 0·4 gram (m. p. 187—188°). It was recrystallised from boiling 2·5 per cent. hydrobromic acid (40 c.c.), and gave 0·35 gram of long, rectangular, chocolate-red leaflets still melting and decomposing at 187—188° (191—192° corr.):

0·1075, air-dried, gave 0·0258 Au.   Au = 24·0.

$C_{17}H_{21}O_4N, AuBr_3, HBr$ requires Au = 24·0 per cent.

l-Hyoscine Picrate.—0·20 Gram of *l*-hyoscine hydrobromide by

double decomposition with a hot-saturated picric acid solution gave
0·25 gram of *l*-hyoscine picrate crystallising in slender, primrose-
yellow needles (m. p. 187—188°). It required a hundred times
its weight of boiling water to dissolve it, and then separated in
flat, irregular, six-sided scales covered with striations. Occasion-
ally, these scales were united in the form of long, flat, serrated
needles. It now melted and decomposed at 187·5—188·5°
(191—192° corr.), and amounted to 0·2 gram.

dl-*Hyoscine.*

dl-*Hyoscine Hydrobromide.*—Two and a-half grams each of the
purest *d*-hyoscine and *l*-hyoscine hydrobromides were combined
and recrystallised from water. The product crystallised exceed-
ingly well with three molecules of water of crystallisation, and was
indistinguishable from the active *d*- or *l*-hyoscine hydrobromides.
The crystals were collected, and amounted to 3·3 grams. In a
capillary tube, the uncrushed crystals melted at 55—58°, but
powdered crystals only partly melted up to 60°, owing to rapid
loss of water. The anhydrous salt melts at 181—182° (185—186°
corr.). The hydrated salt effloresces on exposure to the air, in this
respect differing from the active components. A 2·5 per cent. solu-
tion in water was optically inactive:

0·2217 uneffloresced salt lost 0·0274 in a vacuum. $H_2O = 12·36$.
0·1943, dried in a vacuum, gave 0·0949 AgBr. Br = 20·8.
$C_{17}H_{21}O_4N,HBr,3H_2O$ requires $H_2O = 12·33$ per cent.
$C_{17}H_{21}O_4N,HBr$ requires Br = 20·8 per cent.

dl-*Hyoscine Base.*—One gram of *dl*-hyoscine hydrobromide was
converted into base, using chloroform and sodium hydrogen
carbonate. The chloroform-free base was moistened with water,
and when kept for some hours in a freezing mixture crystallised
in minute needles. The product was collected, washed with water,
and, when dried in the air, amounted to 0·55 gram. It melted at
38—40°:

0·1034, in a vacuum over H_2SO_4, lost 0·0104. $H_2O = 10·1$.
$C_{17}H_{21}O_4N,2H_2O$ requires $H_2O = 10·6$ per cent.

It was recrystallised by dissolving in a little warm alcohol and
adding water until a turbidity developed. On inoculation, it
crystallised slowly in well-formed, transparent, chisel-shaped
prisms. The melting point was unchanged at 38—40° (38—40°
corr.). When dried in a vacuum over sulphuric acid, it lost two
molecules of water:

0·0770 lost 0·0082. $H_2O = 10·6$.

$\quad$ $C_{17}H_{21}O_4N,2H_2O$ requires $H_2O = 10·6$ per cent.

The anhydrous material consisted of a clear varnish, and had no definite melting point.

The melting point of the dihydrate was unchanged after keeping in a Jena-glass tube for ten months.

dl-*Hyoscine Picrate.*—This salt was prepared in aqueous solution by adding a saturated solution of picric acid to a solution of *dl*-hyoscine hydrobromide. An oil separated at first, but was displaced, on warming, by short needles, which melted and decomposed at 173—174°. These were recrystallised from one hundred parts of boiling water, and separated in rosettes of long needles, melting and decomposing at 173·5—174·5° (177·5—178·5° corr.).

The same salt is obtained from the *dl*-base.

dl-*Hyoscine Aurichloride.*—This salt crystallises in long, flat needles with one edge serrated on mixing aqueous solutions of the two components. It melted and decomposed at 214—215°. On recrystallisation from 2·5 per cent. hydrochloric acid, it separated in stout, boat-shaped crystals melting and decomposing at 218—219° (corr.):

0·1175 gave 0·0358 Au.   Au = 30·5.

$\quad$ $C_{17}H_{21}O_4N,AuCl_3,HCl$ requires Au = 30·7 per cent.

dl-*Hyoscine Auribromide.*—On mixing *dl*-hyoscine hydrobromide dissolved in excess of hydrobromic acid with gold chloride solution, this salt crystallises in chocolate-coloured leaflets of indefinite shape melting and decomposing at 209—210°. On recrystallisation from 50 parts of dilute hydrobromic acid solution, it separated in chocolate-red leaflets very similar in appearance to the *laevo*-salt. The melting and decomposing point was unchanged at 213—214° (corr.):

0·1123 gave Au = 0·0268.   Au = 23·9.

$\quad$ $C_{17}H_{21}O_4N,AuBr_3,HBr$ requires Au = 24·0 per cent.

Jowett (*loc. cit.*) has described a hyoscine auribromide melting at 210°, which probably indicates that his starting material, hyoscine hydrobromide, was optically inactive, or practically so.

Hydrolysis of 1-Hyoscine.

With Hydrobromic Acid.—Pure hydrated *l*-hyoscine hydrobromide (1·4447 grams), $[\alpha]_D - 22·7°$ ($c = 2·5$), was dissolved in 30 c.c. of 10 per cent. hydrobromic acid, and the rotation determined. The solution was then boiled gently under reflux, the

rotation being observed at definite intervals by cooling the solution and removing the requisite volume for the observation. On completion of the latter, the solutions were recombined and the boiling started afresh. The following data were obtained, using a 2-dcm. tube:

Initial reading	−141′	After 4 hours' boiling	−159′
After 1 hour's boiling	−149′	,, 6 ,, ,, ...	−161′
,, 2 hours' ,,	−153′	,, 9 ,, ,, ...	−157′

The solution was now thoroughly extracted with purified ether to remove the *l*-tropic acid. The residual aqueous solution still showed a rotation of − 10′, and contained non-hydrolysed hyoscine, as it gave a reaction with Mayer's reagent (oscine gives no reaction in acid solution of this strength). The hydrolysis was continued for a further five hours, when the rotation rose to − 11′, and the reaction for hyoscine was negative. On removal of the *l*-tropic acid by ether, the residual solution was inactive.

The ethereal extracts gave 0·65 gram of crude *l*-tropic acid melting at 125—127° and having $[\alpha]_D - 70·5°$ in water ($c=1$). On recrystallisation from water, it melted at 127—128° and gave $[\alpha]_D - 76°$ ($c=2$).

The *dl*-oscine hydrobromide solution was concentrated rapidly under diminished pressure to a syrup, when it acquired a purple colour, which disappeared on dilution with water, but in absolute alcohol became brown. The syrupy residue crystallised on inoculating with *dl*-oscine hydrobromide. The crude product melted at 270° and weighed 0·75 gram (theory, 0·78). It was triturated with a little absolute alcohol, and the crystals were collected. The product consisted of granular crystals with a violet colour (probably containing traces of a perbromide (compare Schmidt, *Arch. Pharm.*, 1905, **243**, 567), weighed 0·53 gram, and melted at 280°. A mixture with pure *dl*-oscine hydrobromide (m. p. 282°) also melted at 280°. The filtrate was now evaporated to dryness under diminished pressure, dissolved in 10 per cent. sodium hydroxide solution, and completely extracted with chloroform. On removal of the chloroform, 0·15 gram of base was obtained, which only crystallised on inoculation with the *dl*-oscine base of commerce. It melted at 98—100°, and a mixture with pure oscine melted at 103°.

The products of the hydrolysis are therefore *l*-tropic acid and *dl*-oscine.

With Hydrochloric Acid.—Pure *l*-hyoscine base prepared from 0·5014 gram of *l*-hyoscine hydrobromide, $[\alpha]_D - 22·75°$ ($c=2·5$), using sodium hydrogen carbonate and chloroform, was dissolved in

30 c.c. of 10 per cent. hydrochloric acid.   The rotation was followed as in the case of the hydrobromide.

Initial reading .... $-52'$
After 2 hours' boiling .... $-55'$; $l = 2 \cdot$dcm.
,,   4   ,,   ,, ... $-56'$
,,   8   ,,   ,, ... $-54 \cdot 5'$

On removal of the l-tropic acid (0·15 gram; m. p. 124—125°) by ether, the acid aqueous solution was optically inactive, and when evaporated to dryness with absolute alcohol gave 0·13 gram of dl-oscine hydrochloride crystallising in minute, rectangular plates, or associated together in fern-like growths.   It was converted into the picrate, which crystallised in small, flattened rhombs or tablets melting and decomposing at 231°.   A mixture with pure dl-oscine picrate, which crystallises similarly and melts and decomposes at 237—238°, melted intermediately at 232°.

In conclusion, the author desires to express his warmest thanks to Dr. Pyman for his advice and criticism throughout the course of the work.

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XXXVIII.—*The Basic Properties of Oxygen in Organic Acids and Phenols; and the Quadrivalency of Oxygen.*

By JOSEPH KNOX and MARION BROCK RICHARDS.

OXYGEN is usually regarded as a bivalent element in most compounds, but its position in Group VI of the Periodic Table affords good ground for the assumption that it may in certain cases have a higher valency from analogy to sulphur, selenium, and tellurium, all of which may function, not only as bivalent, but also as quadrivalent and sexavalent elements.

The quadrivalency of oxygen has been assumed from time to time to explain the constitution of certain compounds, a summary of the earlier assumptions of this nature being given by Walden (*Ber.*, 1901, **34**, 4185).   The work of Collie and Tickle on

dimethylpyrone (T., 1899, **75**, 710), and of Baeyer and Villiger (*Ber.*, 1901, **34**, 2679; 1902, **35**, 1201), first drew general attention to the subject. The former were of the opinion that only in specially favourable cases could additive compounds containing quadrivalent oxygen be formed, but the latter showed that organic compounds of practically all classes containing oxygen, such as ethers, alcohols, aldehydes, ketones, etc., could combine with acids to give crystalline salts. Since that time, many similar assumptions of the quadrivalency of oxygen have been made, for example, by Bülow and Sicherer for salts of anhydrobenzopyranols and benzopyranols (*Ber.*, 1901, **34**, 3916), by Kehrmann and Mattisson for salts of phenanthraquinone (*Ber.*, 1902, **35**, 343), by Willstätter and Pummerer for compounds of pyrone with acids (*Ber.*, 1904, **37**, 3740), by Farmer for acid salts of monobasic acids (T., 1903, **83**, 1440), by Cohen and Gatecliff for compounds of ethers with nitric acid (P., 1904, **20**, 194; but see also McIntosh, *J. Amer. Chem. Soc.*, 1905, **27**, 1013), by Blaise for compounds of magnesium iodide and zinc iodide with ethers (*Compt. rend.*, 1904, **139**, 1211; 1905, **140**, 661), and by Meyer for salt-like compounds of quinones with acids (*Ber.*, 1908, **41**, 2568).

Much work on this subject has been done by McIntosh and his collaborators, who have prepared additive compounds of ethers, alcohols, aldehydes, ketones, etc., with halogens and anhydrous halogen hydrides (T., 1904, **85**, 919, 1098; 1905, **87**, 784; *J. Amer. Chem. Soc.*, 1905, **27**, 26, 1013; 1906, **28**, 588; 1908, **30**, 1097; 1910, **32**, 542, 1330; 1911, **33**, 70; 1912, **34**, 1273).

Fewer instances have been recorded of the formation of additive compounds of organic acids and phenols with other acids. Baeyer and Villiger obtained no crystalline compounds of acids with acids (*Ber.*, 1901, **34**, 2692). Hoogewerff and van Dorp, however, prepared additive products of sulphuric acid with various organic acids, and of phenols with phosphoric acid (*Rec. trav. chim.*, 1899, **18**, 211; 1902, **21**, 349). Maass and McIntosh obtained a compound of benzoic acid with hydrogen bromide, and of resorcinol with hydrogen bromide and hydrogen chloride (*J. Amer. Chem. Soc.*, 1911, **33**, 70). Pfeiffer also has prepared a number of compounds of organic acids with acids (*Ber.*, 1914, **47**, 1593), and in a recent series of papers Kendall has described the isolation, by the freezing-point method, of additive compounds of organic acids in pairs, of organic acids and phenols with sulphuric acid, and of phenols with organic acids (*J. Amer. Chem. Soc.*, 1914, **36**, 1722, 2498; 1916, **38**, 1309).

It will be seen that the organic compounds which form these

additive products are of the most diverse types. In practically all the cases cited, the organic compound is combined with an acid, forming an unstable additive compound, so that evidently the compound formation is due to basic properties in oxygen of higher valency than two. These additive compounds are generally regarded as "oxonium" compounds, containing quadrivalent oxygen, derived from the hypothetical base $H_3O \cdot OH$, analogous to the sulphonium compounds formed by the passage of sulphur from bivalency to quadrivalency. A typical example is Friedel's dimethyl ether hydrochloride (*Bull. Soc. chim.*, 1875, [ii], **24**, 160): $(CH_3)_2O + HCl = \frac{CH_3}{CH_3}{>}O{<}^{H}_{Cl}$, the analogy of which to a sulphonium compound is evident:

$$(CH_3)_2S + CH_3I \qquad \frac{CH_3}{CH_3}{>}S{<}^{CH_3}_{I}$$
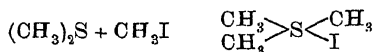
The sulphonium salts are derivatives of the strongly basic sulphonium hydroxide, $R_3S \cdot OH$, so that in the salt-like character of the oxonium compounds, and the basic properties of quadrivalent oxygen, there is a parallel in the case of well-known sulphur compounds.

To explain the formation of these additive compounds, special kinds of valencies of oxygen have from time to time been assumed —crypto-valencies, complex valencies, residual affinities. In view of the fact, however, that oxygen may exhibit a higher valency than two in the ordinarily accepted sense, there seems to be no reason to assign special kinds of valencies to oxygen, any more than to sulphur or the other elements of the same group.

The additive products of organic oxygen compounds with acids have mainly been isolated in the solid state, and very little work has been done on the investigation of these compounds in solution. The compounds are all more or less unstable, and for the most part are decomposed by water into their original constituents. Farmer, for instance, could find no evidence for the existence of acid salts in solution (T., 1903, **83**, 1440), but there is evidence to show that oxonium compounds do exist to a certain extent, at least, in solution. Thus Maass and McIntosh (*J. Amer. Chem. Soc.*, 1913, **35**, 535), by a study of the conductivity measurements of the two component systems—hydrochloric acid and ethyl ether, hydrochloric acid and methyl ether, hydrochloric acid and ethyl alcohol, hydrochloric acid and methyl alcohol—showed the probability of the existence of the compounds in solution. Rördam (*J. Amer. Chem. Soc.*, 1915, **37**, 557), by comparing the conductivity of a solution

of dimethylpyrone hydrochloride with that of a solution of hydrochloric acid with the same concentration of chlorine ions, electrometrically measured, proved that dimethylpyrone hydrochloride is a real salt showing electrolytic dissociation as well as hydrolytic dissociation into its components.   Schuncke (*Zeitsch. physikal. Chem.*, 1894, **14**, 331) found that the solubility of ether is greater in hydrochloric acid solutions than in water, and increases with the concentration of the hydrochloric acid, and Jüttner (*Zeitsch. physikal. Chem.*, 1901, **38**, 56) gave as the reason the formation of ether hydrochloride in solution.   Similarly, Sackur (*Ber.*, 1902, **35**, 1242) found that the solubility of cineole increases in hydrochloric, nitric, and acetic acid solutions.

It is possible, therefore, that the existence of other oxonium compounds in solution may be shown by solubility determinations. If additive compounds of organic acids with acids exist in solution, we should expect to find some influence of this salt-formation on the solubility of the organic acid in solutions of the other acids. If no such disturbing influence comes into play, the solubility of the organic acid should continuously diminish with increasing concentration of the solvent acid, in accordance with the law that the solubility of an electrolyte is diminished by the addition of another electrolyte with a common ion.

A few instances have actually been recorded where organic acids do not obey this law.   Thus, Herz (*Zeitsch. anorg. Chem.*, 1910, **66**, 93) found that for solutions of oxalic acid in boric acid the solubility increases continuously with the concentration of the boric acid.   Stépanov (*Annalen*, 1910, **373**, 221) found that for picric acid in hydrochloric acid solutions the solubility diminishes to a certain point, after which it begins to increase.   Masson (T., 1912, **101**, 103) found a similar result for solutions of oxalic acid in hydrochloric and nitric acid solutions.

It seems very probable that these cases may be instances of a general phenomenon, and that the unexpected results obtained for the solubility curves are caused by the existence in solution of an oxonium compound, formed by direct addition of the ions of the solvent acid to an oxygen atom of the organic acid, according to the equation

$$\frac{R}{HO}\!\!>\!\!C\!:\!O + HX \ = \ \frac{R}{HO}\!\!>\!\!C\!:\!O\!\!<\!\!\frac{H}{X},$$

or, for phenols,

$$\frac{R'}{H}\!\!>\!\!O + HX \qquad \frac{R'}{H}\!\!>\!\!O\!\!<\!\!\frac{H}{X}.$$
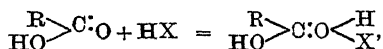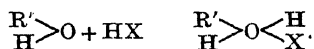
This assumption would be sufficient to account for the observed results. At first with a strong solvent acid, such as hydrochloric or nitric, the effect of the common hydrogen ion prevails, and the solubility diminishes. With increasing concentration of the solvent acid, however, the influence of the formation of the more readily soluble salt becomes stronger, and the solubility reaches a minimum, and finally begins to increase. If the solvent acid is weak, for example, boric acid, the initial decrease may be too small to be measurable; hence the only perceptible effect would be the continuous increase observed by Herz.

If the true explanation of the results observed by Herz, Stépanov, and Masson is the formation of an oxonium compound in solution, we should expect other organic acids to behave in a similar manner, and the present investigation serves to prove that this is actually the case.

Experimental.

I. Acids.

The solubilities of a number of organic acids of practically all classes have been determined in solutions of other acids. The number of organic acids which could be used was greatly limited by the lack of suitable methods of analysis. Many of the commonest acids could not be employed, since no sufficiently accurate method is known for their estimation, or since, even at the ordinary temperature, they volatilise from solution on evaporation. Much time was spent in testing various analytical methods given in the literature for a large number of acids, and in determining whether the acids volatilised from solution on evaporation. Amino-acids were avoided, as the presence of the basic amino-group might lead to the formation of salts of the ammonium type. In most cases, the solvent acid is hydrochloric, but experiments have also been performed in nitric, sulphuric, acetic, formic, and lactic acids.

The following series have been investigated:

Monobasic Acids.—Phenylacetic, diphenylacetic, benzilic, *o*-nitrobenzoic, *m*-nitrobenzoic, 3 : 5-dinitrobenzoic, cinnamic, diphenyleneglycollic, trichlorolactic, mandelic, diphenic, and salicylic acids in hydrochloric acid solutions; trichlorolactic acid in sulphuric acid; mandelic acid in sulphuric, acetic, and formic acids.

Dibasic Acids.—Malonic acid in hydrochloric and sulphuric acids; oxalic acid in sulphuric, acetic, formic, and lactic acids;

phthalic acid in hydrochloric and nitric acids; suberic acid in hydrochloric, nitric, sulphuric, and acetic acids; succinic acid in hydrochloric, nitric, sulphuric, acetic, and formic acids; and tartaric acid in hydrochloric, sulphuric, and acetic acids.

Tribasic Acid.—Citric acid in hydrochloric and sulphuric acids.

Method.—The solubilities were determined at 25°, excess of the solid being shaken for several days in a thermostat with solutions of the solvent acid of varying concentration. After saturation, the clear solution was analysed both for dissolved and solvent acid by one of the following methods:

(1) Solvent acid determined gravimetrically; dissolved acid by direct weighing after evaporation in a vacuum over soda-lime.

This method was used for most of the sparingly soluble acids in hydrochloric acid solutions.

(2) Total acidity determined by titration with standard sodium hydroxide; dissolved acid by weighing after evaporation either (*a*) in a vacuum, or (*b*) on the steam-bath; solvent acid by difference.

This method was used for nitric, acetic, and formic, and in a few cases for hydrochloric, acid solutions.

(3) Total acidity by titration; solvent acid gravimetrically; dissolved acid by difference.

Sulphuric acid solutions were analysed by this method, also cases of acids very readily soluble in hydrochloric acid.

(4) Permanganate methods for oxalic acid solutions: total acidity by alkali; oxalic acid by potassium permanganate, either (*a*) directly, in sulphuric acid solutions, or (*b*) after precipitation as calcium oxalate in other cases; solvent acid by difference.

Where an evaporation method was used, a preliminary test was made to ascertain whether the organic acid was left unchanged after evaporation from a solution in the solvent acid.

The results of the various experiments are given in the following tables. The method of analysis is indicated in each case by a number corresponding with the above arrangement, and reference is made to the diagram in which the corresponding solubility curve is to be found. In all cases, the concentrations of the acids are expressed in equivalent normalities. .

(1) *Phenylacetic Acid in Hydrochloric Acid. Method 1. Fig. 1.*

HCl	0	1·417	2·890	4·313	5·770	7·175	8·590	9·988	11·36
$C_8H_8O_2$	0·1310	0·0984	0·0833	0·0763	0·0739	0·0756	0·0815	0·0916	0·1099

(2) *Diphenylacetic Acid in Hydrochloric Acid. Method 2(b).*

HCl	0	1·620	2·913	4·512	5·973	7·349	8·889	10·27	11·74
$C_{14}H_{12}O_2$	0·00060	0·00047	0·00040	0·00036	0·00038	0·00041	0·00042	0·00046	0·00053

(3) *Benzilic Acid in Hydrochloric Acid. Method 2(b).*

HCl	0	1·537	2·977	4·440	5·934	7·356	8·803	10·25	11·69
$C_{14}H_{12}O_3$	0·00769	0·00332	0·00233	0·00182	0·00172	0·00150	0·00167	0·00195	0·00217

(4) *o-Nitrobenzoic Acid.* Method 1.

HCl	0	1·314	2·607	3·909	5·013	6·509	7·795	9·080	10·30
$C_7H_5O_4N$	0·0470	0·0280	0·0256	0·0239	0·0235	0·0233	0·0237	0·0250	0·0267

(5) *m-Nitrobenzoic Acid in Hydrochloric Acid. Method 1.*

HCl	0	1·416	3·310	4·308	5·953	7·044	8·380	9·793	11·54
$C_7H_5O_4N$	0·0214	0·0175	0·0178	0·0183	0·0205	0·0225	0·0256	0·0293	0·0368

* It may be mentioned that Kendall (*Proc. Roy. Soc.*, 1911, [A], **85**, 200) gives results for the solubilities of o-nitrobenzoic acid, and salicylic acid, in hydrochloric acid solutions; but with the low concentrations of hydrochloric acid used in his experiments, only the decrease in solubility is observed.

(6) 3:5-Dinitrobenzoic Acid in Hydrochloric Acid. Method 2(b).

HCl	0	1·565	2·908	4·594	5·657	7·336	8·855	10·27	11·73
$C_7H_4O_6N_2$	0·00635	0·00398	0·00470	0·00583	0·00690	0·00841	0·00965	0·01095	0·01240

(7) Cinnamic Acid in Hydrochloric Acid. Method 1.

HCl	0	2·100	4·174	6·250	8·007	10·29	10·47
$C_9H_8O_2$	0·00385	0·00283	0·00272	0·00318	0·00400	0·00556	0·00572

(8) Diphenyleneglycollic Acid in Hydrochloric Acid. Method 2(b).

HCl	0	1·952	3·907	5·843	7·745
$C_{14}H_{10}O_3$	0·01082	0·00492	0·00355	0·00343	0·00352

(9) Trichlorolactic Acid in Hydrochloric Acid. Method 3.

HCl	0	1·234	2·837	4·388	5·982	7·675	8·959	10·65	11·86	12·17
$C_3H_3O_3Cl_3$	4·024	2·545	1·425	0·984	0·760	0·659	0·624	0·57	0·57	0·60

(10) Trichlorolactic Acid in Sulphuric Acid. Method 3.

H_2SO_4	0	2·525	6·166	9·588	12·75	16·28	19·38	22·28	25·34
$C_3H_3O_3Cl_3$	4·024	1·896	0·671	0·353	0·26	0·15	0·18	0·21	0·26

(11) Salicylic Acid in Hydrochloric Acid.* Method 1.

HCl	0	1·459	3·057	4·374	6·164	7·311	8·730	10·20	11·54	12·20
$C_7H_6O_3$	0·01613	0·00982	0·00822	0·00715	0·00654	0·00656	0·00866	0·00710	0·00794	0·00856

* See footnote on preceding page.

(12) Diphenic Acid in Hydrochloric Acid. Method 2(b).

HCl	0	2·103	3·985	5·928	7·748
$C_{14}H_{10}O_4$	0·00520	0·00182	0·00144	0·00112	0·00118

(13) Mandelic Acid in Hydrochloric Acid. Method 1. Fig. 2.

HCl	0	1·202	2·481	3·753	5·017	6·271	7·523	8·748	9·937	10·35
$C_8H_8O_3$	1·191	0·691	0·488	0·387	0·532	0·307	0·302	0·316	0·353	0·375

(14) Mandelic Acid in Sulphuric Acid. Method 3. Fig. 2.

H_2SO_4	0	2·695	5·390	8·294	11·05	13·62	16·50	18·89	21·17
$C_8H_8O_3$	1·191	0·484	0·278	0·186	0·18	0·18	0·16	0·23	0·27

(15) Mandelic Acid in Acetic Acid. Method 2(a). Fig. 2.

$C_2H_4O_2$	0	0·870	1·338	1·860	2·618	3·644	4·249	4·738	6·485	8·60	9·85	12·30
$C_8H_8O_3$	1·191	1·808	2·312	2·664	3·186	3·444	3·472	3·487	3·509	3·234	2·996	2·178

(16) Mandelic Acid in Formic Acid. Method 2(a). Fig. 2.

CH_2O_2	0	2·268	4·340	6·320	8·09	10·38	12·20	13·41	13·78
$C_8H_8O_3$	1·191	1·768	2·180	2·383	2·430	2·434	2·525	2·750	3·327

(17) Malonic Acid in Hydrochloric Acid. Method 3. Fig. 3.

HCl	0	4·443	6·210	8·658	10·47	11·09	11·22
$C_3H_4O_4$	15·01	7·70	5·99	4·71	4·32	4·26	4·30

(18) Malonic Acid in Sulphuric Acid. Method 3. Fig. 3.

H_2SO_4	0	2·727	7·050	11·76	16·05	19·92	21·84
$C_3H_4O_4$	15·01	11·44	6·79	4·07	3·01	3·20	4·55

(19) Oxalic Acid in Sulphuric Acid. Method 4(a). Fig. 4.

H_2SO_4	0	2·187	4·524	6·835	9·225	11·45	13·63	15·57	17·15
$C_2H_2O_4$	2·409	1·519	1·057	0·791	0·675	0·691	0·830	1·157	1·804

(20) Oxalic Acid in Lactic Acid. Method 4(b). Fig. 4.

$C_3H_6O_3$	0	1·337	2·718	4·051	5·357	6·477	7·647	8·709	9·52
$C_2H_2O_4$	2·409	2·228	2·054	1·856	1·633	1·412	1·171	0·938	0·832

(21) Oxalic Acid in Formic Acid. Method 4(b). Fig. 4.

CH_2O_2	0	0·097	0·437	0·967	1·287	1·825	2·678	5·360	8·13	11·00	12·17	16·63	19·25	21·11
$C_2H_2O_4$	2·409	2·382	2·385	2·411	2·414	2·441	2·430	2·326	2·131	1·868	1·758	1·496	1·568	2·339

(22) Oxalic Acid in Acetic Acid. Method 4(b). Fig. 4.

$C_2H_4O_2$	0	0·135	0·321	0·923	1·361	1·844	5·721	8·005	8·563	9·864	12·55	14·03	14·21	14·83
$C_2H_2O_4$	2·409	2·356	2·361	2·395	2·402	2·401	2·168	1·839	2·351	1·546	1·100	0·896	0·875	0·802

(23) Phthalic Acid in Hydrochloric Acid. Method 1.

HCl	0	1·729	3·113	4·693	6·100	7·603	9·150	10·63	12·05
$C_8H_6O_4$	0·0852	0·0422	0·0298	0·0216	0·0172	0·0135	0·0120	0·0128	0·0137

(24) *Phthalic Acid in Nitric Acid. Method 2(a).*

HNO₃	0	2.077	4.077	6.718	9.027	10.40	12.60	14.42	15.99
C₈H₆O₄	0.0852	0.0582	0.0470	0.0375	0.0331	0.0325	0.0350	0.0420	0.0577

(25) *Suberic Acid in Hydrochloric Acid. Method 1. Fig. 1.*

HCl	0	1.423	2.858	4.281	5.691	7.130	8.378	9.865	11.20
C₈H₁₄O₄	0.0680	0.0498	0.0428	0.0412	0.0432	0.0504	0.0633	0.0905	0.1370

(26) *Suberic Acid in Nitric Acid. Method 2(a).*

HNO₃	0	0.307	0.555	0.906	1.543	2.021	4.035	5.749	8.091	10.05	11.77	13.30
C₈H₁₄O₄	0.0680	0.0594	0.0590	0.0634	0.0695	0.0839	0.0999	0.1133	0.1575	0.2231	0.3896	0.6049

(27) *Suberic Acid in Sulphuric Acid. Method 3.*

H₂SO₄	0	1.858	5.233	7.524	11.33	18.65
C₈H₁₄O₄	0.068	0.039	0.037	0.042	0.06	0.20

(28) *Suberic Acid in Acetic Acid. Method 2(a).*

C₂H₄O₂	0	0.435	0.887	2.112	4.262	6.350	8.402
C₈H₁₄O₄	0.0680	0.0776	0.0902	0.1340	0.2891	0.4317	0.5846

(29) *Succinic Acid in Hydrochloric Acid. Method 1. Fig. 5.*

HCl	0	2.751	5.964	7.335	8.950	9.732	10.40	11.98
C₄H₆O₄	1.352	0.681	0.402	0.353	0.333	0.328	0.337	0.378

(30) Succinic Acid in Nitric Acid. Method 2(a). Fig. 5.

HNO_3	0	1·299	3·034	5·236	6·616	9·710	11·11	13·51	15·43
$C_4H_6O_4$	1·352	1·134	0·941	0·724	0·652	0·528	0·518	0·561	0·731

(31) Succinic Acid in Sulphuric Acid. Method 3. Fig. 5.

H_2SO_4	0	1·981	3·816	4·926	8·122	10·22	13·81	17·05	20·28	23·18
$C_4H_6O_4$	1·352	0·908	0·683	0·563	0·388	0·34	0·30	0·30	0·39	0·69

(32) Succinic Acid in Acetic Acid. Method 2(a). Fig. 5.

$C_2H_4O_2$	0	0·078	0·448	0·916	2·828	4·536	6·655	8·661	10·34	12·40	14·64	16·85
$C_4H_6O_4$	1·352	1·384	1·415	1·452	1·592	1·643	1·639	1·519	1·357	1·097	0·797	0·514

(33) Succinic Acid in Formic Acid. Method 2(a). Fig. 5.

CH_2O_2	0	0·090	0·446	0·930	3·730	5·547	7·500	11·29	15·29	17·67	19·16	20·53	22·93
$C_4H_6O_4$	1·352	1·369	1·397	1·408	1·601	1·531	1·449	1·228	0·944	0·796	0·715	0·667	0·604

(34) Tartaric Acid in Hydrochloric Acid. Method 3. Fig. 6.

HCl	0	1·257	2·568	4·466	6·303	8·144	9·890	10·51	11·17
x $C_4H_6O_6$	10·26	8·528	7·092	5·434	4·35	3·77	3·43	3·42	3·42

(35) Tartaric Acid in Sulphuric Acid. Method 3. Fig. 6.

| SO_4 .... | 0 | 1·798 | 4·043 | 6·807 | 9·895 | 12·54 | 15·46 | 18·10 | 19·85 | 22·17 |
| $C_4H_6O_6$ .... | 10·26 | 8·51 | 6·64 | 4·73 | 3·18 | 2·43 | 1·95 | 1·77 | 1·86 | 2·74 |

(36) Tartaric Acid in Acetic Acid. Method 2(a). Fig. 6.

| $C_2H_4O_2$ .... | 0 | 0·25 | 0·60 | 1·23 | 2·63 | 4·24 | 6·12 | 8·30 | 10·89 | 14·14 | 16·92 |
| $C_4H_6O_6$ .... | 10·26 | 10·09 | 9·875 | 9·515 | 8·717 | 7·718 | 6·548 | 5·151 | 3·505 | 1·594 | 0·344 |

(37) Citric Acid in Hydrochloric Acid. Method 3.

| HCl .... | 0 | 0·949 | 2·189 | 3·795 | 5·718 | 7·736 | 9·635 | 10·36 | 11·09 |
| $C_6H_8O_7$ .... | 12·54 | 11·03 | 9·30 | 7·36 | 5·38 | 4·09 | 3·46 | 3·35 | 3·29 |

(38) Citric Acid in Sulphuric Acid. Method 3.

| H_2SO_4 .... | 0 | 1·689 | 4·206 | 7·145 | 10·83 | 11·46 | 14·24 | 18·18 | 20·59 | 22·37 |
| $C_6H_8O_7$ .... | 12·54 | 10·57 | 7·97 | 5·61 | 3·28 | 3·07 | 2·23 | 1·76 | 2·00 | 2·88 |

(39) p-Nitrophenol in Hydrochloric Acid. Method 5(a). Fig. 7.

| HCl .... | 0 | 1·660 | 3·277 | 4·993 | 6·552 | 8·196 | 9·817 |
| $C_6H_5O_3N$ ...... | 0·1097 | 0·0962 | 0·0913 | 0·0934 | 0·0990 | 0·1093 | 0·1230 |

(40) *m-Nitrophenol in Hydrochloric Acid. Method 5(a). Fig. 7.*

HCl	0	1·025	3·822	5·720	7·550	9·213	10·96	11·20
$C_6H_6O_3N$	0·0974*	0·0849	0·0884	0·0886	0·1009	0·1130	0·1284	0·1307

(41) *Picric Acid in Nitric Acid. Method 6(b).*

HNO_3	0	1·022	2·059	4·161	6·289	8·334	10·47	12·47	14·29
$C_6H_3O_7N_3$	0·0578	0·0108	0·0124	0·0237	0·0405	0·0612	0·1006	0·1763	0·3853

(42) *β-Naphthol in Hydrochloric Acid. Method 5(a).*

HCl	0	1·466	2·952	4·343	5·785	7·122	8·674	11·47
$C_{10}H_8O$	0·00524	0·00410	0·00360	0·00333	0·00319	0·00316	0·00307	0·00341

(43) *Resorcinol in Hydrochloric Acid. Method 5(a).*

HCl	0	0·656	1·671	3·410	4·402	6·076	7·567	9·157	9·610	11·31
$C_6H_6O_2$	6·515	5·705	4·570	3·020	2·307	1·616	1·287	1·125	1·118	1·389

* It may be remarked that the value found for the solubility of *m*-nitrophenol in water differs considerably from that given by Vaubel (*J. pr. Chem.*, 1895, [ii], 52, 73), but as no definite particulars are given of the method employed, or of the source of his result, it cannot be regarded as very trustworthy. The compound used in the present case, which was prepared from *m*-nitroaniline, was recrystallised from water, and melted at 96—97°.

(44) Quinol in Hydrochloric Acid. Method 5(a).

HCl	0	1·892	3·793	5·729	7·597	9·237	10·97
$C_6H_4O_2$	0·666	0·402	0·282	0·215	0·188	0·178	0·166

(45) Catechol* in Hydrochloric Acid. Method 5(a).

HCl	0	1·68	3·53	5·39	7·30	9·11	10·83
$C_6H_4O_2$	4·19	2·13	1·18	0·81	0·62	0·55	0·55

(46) Styphnic Acid in Hydrochloric Acid. Method 5(b).

HCl	0	1·410	2·814	4·221	5·634	6·997	8·418	11·10	11·16
$C_6H_3O_8N_3$	0·02179	0·00062	0·00060	0·00072	0·00093	0·00163	0·00197	0·00379	0·00387

(47) Styphnic Acid in Nitric Acid. Method 6(a).

HNO₃	0	1·785	4·171	6·234	8·368	10·31	11·97	13·97	15·57
$C_6H_3O_8N_3$	0·02179	0·001403	0·002180	0·003274	0·005108	0·007944	0·01298	0·02742	0·05611

(48) Pyrogallol in Hydrochloric Acid. Method 5(a).

HCl	0	1·53	3·18	5·12	6·86	8·68	10·43	10·48
$C_6H_6O_3$	4·02	2·81	1·86	1·26	1·01	0·91	0·92	0·93

* The preliminary test showed that catechol is very slightly volatile at the ordinary temperature in a vacuum, but the regularity of the curve obtained seems to show that in spite of this the results are fairly accurate.

II. *Phenols.*

The solubility of a number of phenols has been determined in the same way, the series investigated being:

Monohydric Phenols.—p-Nitrophenol, m-nitrophenol, and β-naphthol in hydrochloric acid; trinitrophenol (picric acid) in nitric acid.

Dihydric Phenols.—Resorcinol, quinol, catechol, and trinitroresorcinol (styphnic acid) in hydrochloric acid; trinitroresorcinol in nitric acid.

Trihydric Phenol.—Pyrogallol in hydrochloric acid.

Methods of Analysis.—5. For all phenols in hydrochloric acid, the acid was determined gravimetrically, and the phenol by weighing after evaporation (*a*) in a vacuum, or (*b*) on the steam-bath.

6. For picric acid and styphnic acid in nitric acid, the concentrations of the nitric acid solutions were determined at 25° before adding the solid, owing to the difficulty of titrating solutions containing these phenols. As the phenols are only sparingly soluble, however, any change in volume that might occur when they dissolve could have no appreciable effect on the results. The phenol was determined by weighing, after evaporation (*a*) in a vacuum, or (*b*) on the steam-bath.

Some of the phenols gave deeply coloured solutions, but the residues obtained on. evaporation were practically colourless, and a preliminary experiment showed that they were left unchanged when evaporated to dryness with hydrochloric acid or nitric acid.

The results are given in tables 39 to 48, the solubilities of the phenols being given in gram-molecules per litre, whilst the concentrations of the solvent acid are expressed, as before, in equivalent normalities.

Consideration of Results.

A glance at the solubility curves will suffice to show that the results observed by Herz, Stépanov, and Masson were no isolated phenomena, but that, as regards the solubility of organic acids and phenols in solutions of other acids, deviation from Nernst's law is the rule and not the exception. It will be seen that the curves obtained are of two main types, according as the solvent acid is a mineral or an organic acid, but in each case the assumption of oxonium salt-formation is sufficient to account for the observed results.

Owing to exigencies of space, only a few typical solubility curves can be reproduced. The other solubility curves, which can be

constructed from the tables, will be referred to by the number of the table containing the necessary data. Thus (1) refers to the solubility of phenylacetic acid in hydrochloric acid, and so on.

The curves obtained for solutions in the mineral acids all resemble more or less those obtained by Stépanov and Masson, that is, the solubility diminishes rapidly at first, reaches a minimum, and afterwards increases steadily with increasing concentration of the solvent acid. The results, however, vary somewhat according

FIG. 1.

Normality of solvent acid.
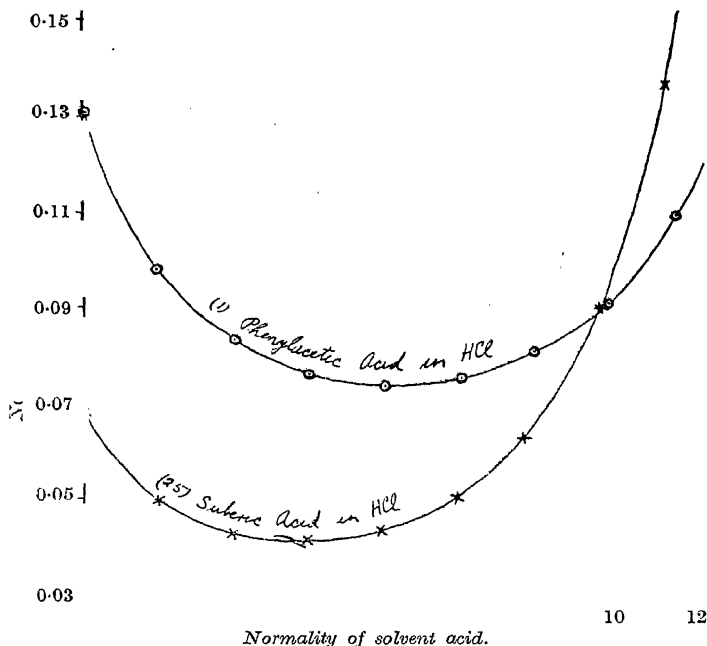
to the solubility of the organic acid or phenol, and the concentrations attainable with the mineral acid. Thus with sparingly soluble acids and phenols, such as phenylacetic (1, 25, Fig. 1) and nitrobenzoic acids (4, 5), and the nitrophenols (39, 40, Fig. 7), the curve in every case shows a distinct turning point. Other examples are 2, 3, 6, 7, 8, 11, 12, 23, 24, 25, 26, 27, 39, 40, 41, 42, 46, 47. With very readily soluble substances, such as malonic, citric, and tartaric acids, quinol, and catechol (17, Fig. 3), (34,

Fig. 6), (37, 43, 44, 45, 48), the concentration of hydrochloric acid reached is not sufficient to show clearly the upward tendency of the curve, although the general shape makes it evident that the

FIG. 2.
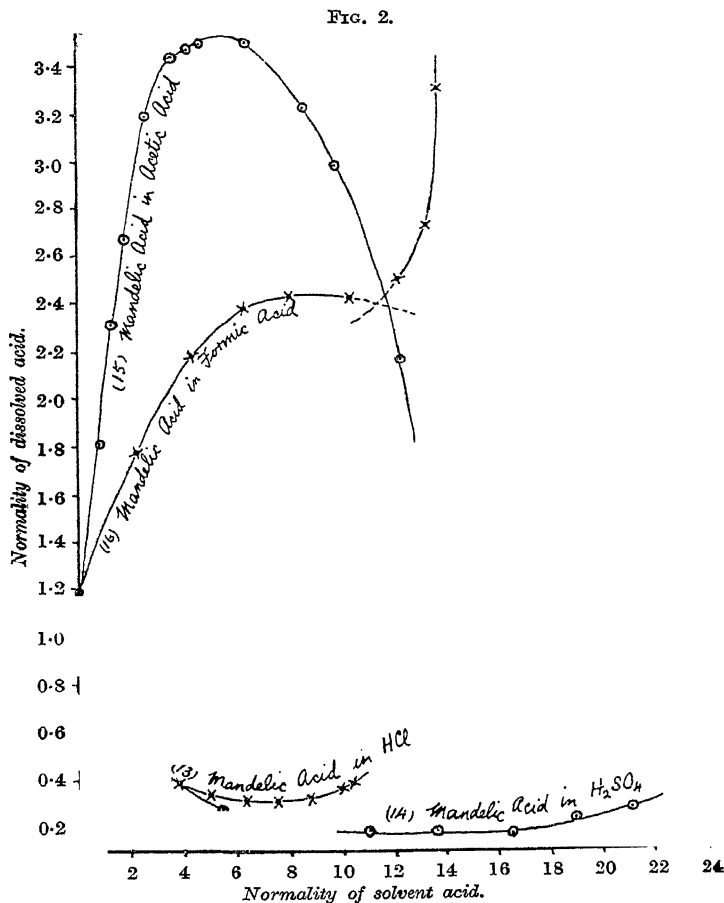
curve has reached its minimum at the concentration attained, and is just about to turn upwards—a conclusion which is further justified by the fact that in sulphuric acid solutions, where the concentrations attainable are considerably greater, even the very

readily soluble acids give a definite turning point (18, Fig. 3), (35, Fig. 6), (38).

When the solvent acid is organic, modification of the shape of the curve results from two causes, namely, (*a*) the weakness of organic acids in general, and (*b*) the wide difference between the

FIG. 3.

Normality of solvent acid.
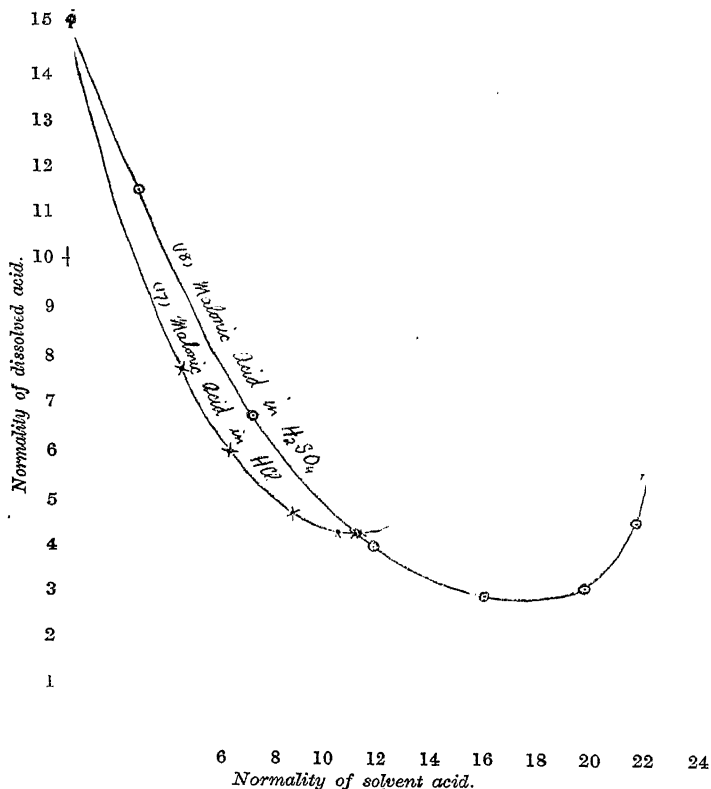
solubilities of the dissolved acid in water and in the organic acid solvent.

(*a*) When both solvent and dissolved acids are weak, the effect of the common hydrogen ion is, as a rule, too small to be measured. Of the acids the solubilities of which were determined in an organic acid solution, oxalic acid is the only one of sufficient acidic strength

to show any perceptible initial decrease in solubility (21, 22, Fig. 4). The others show increase in solubility from the beginning, except tartaric in acetic (36, Fig. 6), and oxalic in lactic acid (20, Fig. 4), where no evidence of salt-formation was obtained.

(*b*) If the dissolved acid is more readily soluble in the solvent organic acid than in water, the resulting curve shows a continuous increase—an increase which may be partly due to salt-formation or entirely due to increasing solubility in the solvent acid, so that

FIG. 4.

Normality of solvent acid.
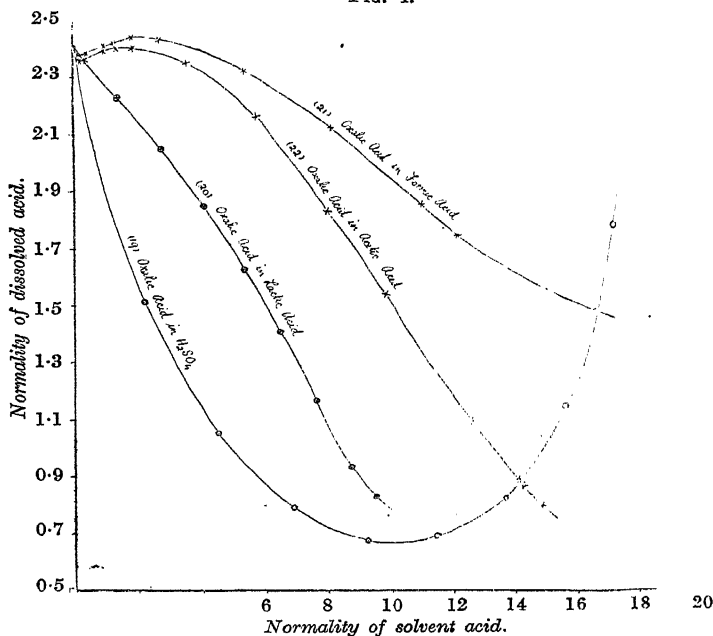
no conclusion as to salt-formation can be drawn. An instance of this may be seen in the curve for suberic acid in acetic acid (28). Other cases give clear evidence of salt-formation, the curve showing an initial increase in solubility, owing to the formation of the more readily soluble salt, with a subsequent decrease, caused by decreasing solubility in the solvent acid. The curves which show this effect clearly are: (1) succinic acid in acetic and formic acids (32, 33, Fig. 5); (2) oxalic acid in acetic and formic acids (here the ionic effect is first perceptible, before the increase due to salt-

formation) (21, 22, Fig. 4), and (3) mandelic acid in acetic and formic acids (15, 16, Fig. 2).

(It will be observed that in three of these cases, namely, oxalic acid in acetic and formic acid solutions, and mandelic acid in formic acid, there is apparently a break in the curve. The cause of this has not been investigated, but Masson, who obtained a similar break for oxalic acid in nitric acid, attributed the result to dehydration of the oxalic acid.)

FIG. 5.

Normality of dissolved acid.
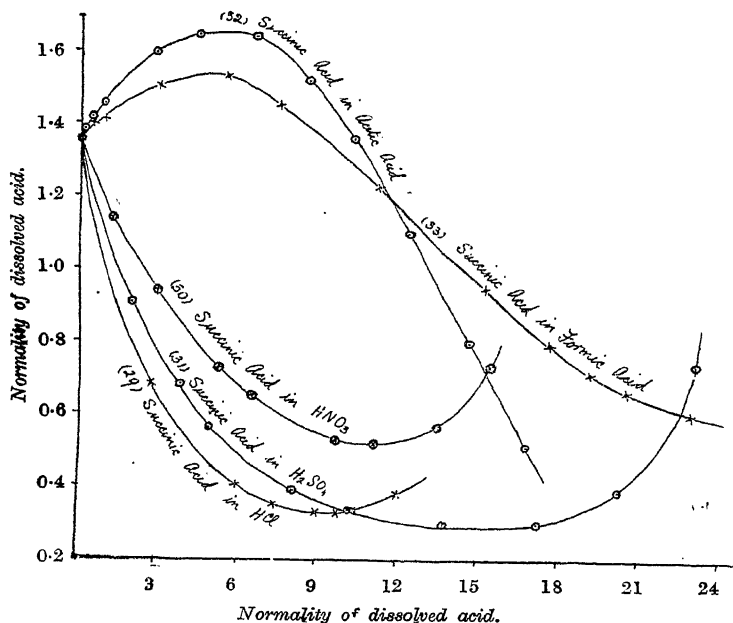
From the curves, it may be inferred that salt-formation does not take place with equal readiness in all the mineral acids. Where curves have been determined for the same organic acid or phenol both in hydrochloric and nitric acid solutions, it will be seen that in each case the nitric acid curve lies above that for hydrochloric acid, evidently indicating that additive compounds are formed more readily with nitric acid; see, for example, the curves for succinic (29, 30, Fig. 5), phthalic (23, 24), suberic (25, 26), and

styphnic acids (46, 47) in hydrochloric and nitric acid respect-
ively.

Again, a comparison of the curves for the same acid in hydro-
chloric and sulphuric acid solutions shows uniformity of behaviour
in all the cases investigated. There is at first a more rapid
decrease in solubility in hydrochloric than in sulphuric acid (prob-
ably due to the greater acidic strength of hydrochloric acid, and
the correspondingly greater ionic effect), but the turning point is
more quickly reached and the hydrochloric acid curve soon cuts
the other, from which we may infer that salt-formation takes place
with greater ease in hydrochloric acid. A comparison of the curves
for succinic (29, 31, Fig. 5), citric (37, 38), tartaric (34, 35, Fig. 6),

Fig. 6.

Normality of solvent acid.
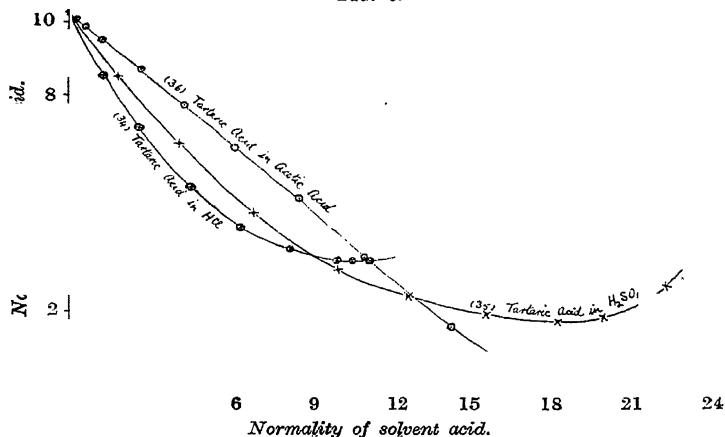
malonic (17, 18, Fig. 3), mandelic (13, 14, Fig. 2), and trichloro-
lactic acids (9, 10) in hydrochloric and sulphuric acids, respectively,
will make this clear. (In the case of suberic acid [25, 27], the
result appears to be similar, but owing to the small solubility of
suberic acid, and the necessity for estimating the suberic acid in
sulphuric acid solutions by difference, this curve is not sufficiently
accurate to enable the distinction between the two curves to be
clearly seen.) It would therefore appear that, of the mineral
acids, sulphuric acid shows the least tendency to salt-formation,
whilst nitric acid shows the greatest.

No quantitative connexion can be established between the turn-
ing point of the curve and the strength of the organic acid in

x* 2

question. Kendall found that, in general, for additive compounds, both of organic acids in pairs and of organic acids with sulphuric acid, the tendency towards the formation of additive compounds is dependent on the difference in acidic strengths. Very weak organic acids most readily form additive compounds, and an

FIG. 7.

Normality of solvent acid.
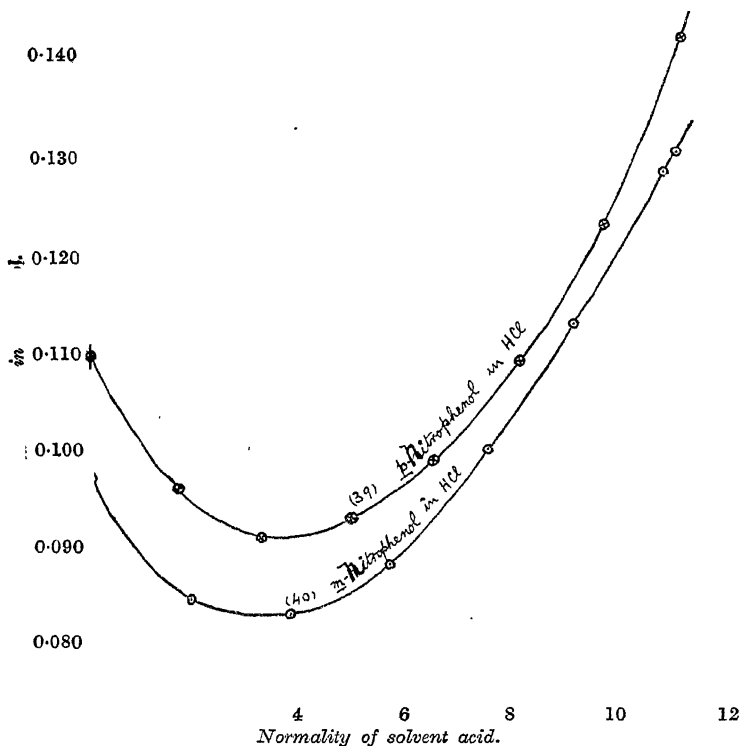
increase in the acidic strength is accompanied by a diminution or loss of this property. The rule is, however, merely qualitative. This result is, in general, confirmed by the present investigation, although the question is complicated by the fact that the turning point in the solubility curve depends largely on the solubility of the organic acid.

General Summary of Results.

From determinations of the solubility of organic acids and phenols in solutions of other acids, it has been shown that in such solutions compounds are formed between the organic acid or phenol and the solvent acid. The most probable explanation is that the organic acids and phenols contain a basic oxygen atom, and that this forms salts of the oxonium type with the solvent acid, the oxygen becoming quadrivalent. This view is strongly supported by the work of Kendall, whose earlier papers were published during the progress of the present research.*

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XXXIX.—ψ-1 : 8-iso*Naphthoxazones.*

By BIMAN BIHARI DEY and MAHENDRA NATH GOSWAMI.

BY the fusion of a pyridine with a benzene nucleus, the condensed quinoline ring is formed, and in a similar manner it is conceivable that the coumarin ring would give rise to a class of derivatives which might be represented as ψ-β-naphthoxazones,† their relation-

* Kendall has since published other papers on the same subject, reference to which will be found in the concluding paper of the series (*J. Amer. Chem. Soc.*, 1917, **39**, 2303), in which he sums up the results of his investigations The above research was completed early in 1916, but for various reasons publication of the results has been delayed.

† As the compounds described in this paper do not contain the true oxazine ring, they are regarded as being derived from ψ-naphthoxazines, thus :
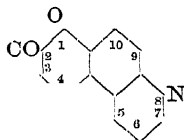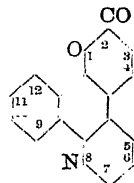
ψ-1 : 8-*iso*Naphthoxazone.   ψ-Benzo-1 : 8-*iso*naphthoxazone.

Isomerides of ψ-1 : 8-*iso*naphthoxazone will thus receive the name :
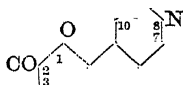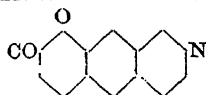
ψ-1 : 8-α-Naphthoxazone.   ψ-1 : 8-β-Naphthoxazone.

ship to coumarins being analogous to that of quinoline to benzene:

O
CO
→
O
CO
N
.
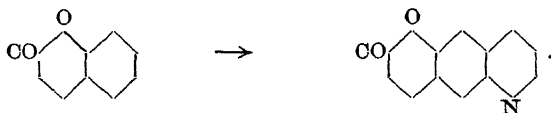
Substances of the latter class, so far as it has been possible to ascertain, are practically unknown, only one instance being encountered in the literature where a compound probably belonging to this category has been mentioned (Pechmann and Schwarz, *Ber.*, 1899, **32**, 3701). This substance was obtained as a by-product in the condensation of *m*-aminophenol and ethyl acetoacetate, where, in addition to the expected 7-amino-4-methylcoumarin, a small amount of a solid (m. p. 268°) was isolated, which was regarded as a dihydroquinocoumarin, and assigned the following structure:

O   N
CO   Me
Me   Me₂
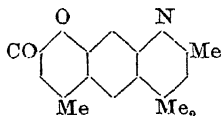
The evidence adduced in favour of its constitution is not complete, and no further work appears to have been carried out on the subject.

The reactions which are of general applicability in the synthesis of quinoline and its allies, namely, the Skraup, the Doebner-Miller, and the Knorr reactions, are all based on the condensations of aniline or other primary aromatic amines; the same methods, with slight modifications, have now been applied to the synthesis of the ψ-naphthoxazones from the aminocoumarins and the aminonaphthacoumarins, in which the amino-groups are attached to the benzene nucleus. These compounds have been shown by previous investigators to resemble the aromatic amines in their chemical behaviour; and they may readily be diazotised and reduced to the corresponding coumarylhydrazines, etc. (Morgan and Micklethwait, T., 1904, **85**, 1233; Clayton, P., 1911, **27**, 246).

These considerations led to the present investigation, a systematic study of this new class of substances being also considered desirable in view of certain questions that arose with regard to the connexion between their structure and physiological properties.

The present communication deals with the application of the Skraup synthesis to the preparation of the ψ-naphthoxazones, the

results obtained with the other reactions being incomplete and reserved for a future communication.

The Skraup reaction, which depends on the condensation of aromatic amines with glycerol and sulphuric acid in the presence of an oxidising agent, is apt to be rather violent when applied to the aminocoumarins, and it was found that the success of the operation depended to a great extent on the careful regulation of the temperature at the commencement of the reaction. It was also observed that, instead of using a mixture of nitro- and amino-coumarins, as is generally done in these reactions, the nitro-coumarins could be employed alone, without diminishing the yield of the ψ-naphthoxazones to any appreciable extent.

This observation greatly simplified the process of this synthesis, as the aminocoumarins were sometimes rather difficult to prepare from the corresponding nitro-compounds.

On treating 6-nitrocoumarin with allyl alcohol, it was reduced to the amino-compound (compare Brunner and Chuard, *Ber.*, 1885, **18**, 447), and it may therefore be legitimately assumed that allyl alcohol is formed in one of the stages in the condensation and is then oxidised to the corresponding aldehyde by the nitro-compound, which is reduced in the process. The amino-compound now serves to combine with the acraldehyde, after which the reaction takes the usual course:
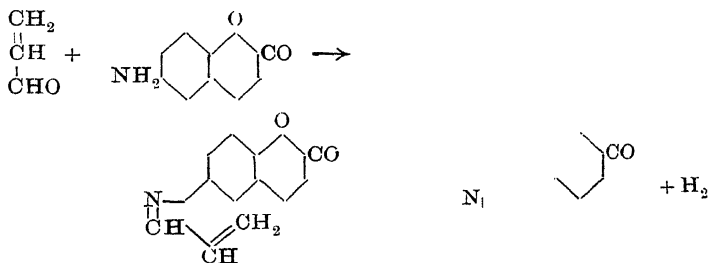
In their chemical characteristics, the ψ-naphthoxazones do not differ materially from the quinolines, except in their behaviour towards hot alkali hydroxides, which dissolve these substances with a deep colour. This is evidently due to the hydrolysis of the pyrone ring, and the solution presumably contains an unstable acid; on carefully neutralising the alkaline solution in the cold, the original substance is slowly deposited in the crystalline state.

The ψ-naphthoxazones, as tertiary bases, readily form salts, a large variety of the double salts having been prepared in the course of this investigation; amongst these, the dichromates, the

ferrocyanides, and the double potassium mercuri-iodides are very characteristic and form crystals having a definite structure. They also give characteristic precipitates with the general alkaloidal reagents: Wagner's solution gives a deep orange-brown, crystalline precipitate of the iodide, Scheibler's reagent gives a white, crystalline precipitate of the phosphotungstates, and Sonnenschein's reagent gives a curdy precipitate of the corresponding phosphomolybdate.

Like the tertiary amines, they also unite with alkyl haloids in molecular proportions. A feature of some interest which has arisen from a study of these N-alkyl iodides is the remarkable phenomenon of colour exhibited by members of the series in the solid state and in solution. Although the ψ-naphthoxazones are generally colourless, and form colourless solutions in dilute mineral acids, their additive products with the alkyl iodides possess a deep colour varying in shade from dark yellow to scarlet-red. The aqueous solutions of these iodides, however, which are strongly ionised, are practically colourless.

In seeking an explanation for this behaviour, the influence of ionisation, and also, perhaps, that of the alkyl group and the halogen, has to be taken into account, and it seems feasible, therefore, to suggest that the ions, basic and acidic, are colourless, whilst the undissociated molecule of the N-alkyl iodide is intensely coloured.

If, moreover, this interpretation is correct, it would be reasonable to expect that the solutions of these iodides in non-ionising media would be coloured. This has been observed to be the case, for although the ordinary non-ionising solvents, like benzene, chloroform, etc., were found to have little or no solvent action on these iodides, the latter dissolved in warm toluene or xylene, the solutions being generally purple with an intense pink fluorescence.

In the reduction of the ψ-naphthoxazones, the pyridine ring is first hydrogenised. The N-tetrahydro-ψ-naphthoxazones crystallise in golden-yellow needles, and their chemical behaviour coincides exactly with that of the fatty, aromatic secondary amines; the presence of the imino-group in their molecules is shown by the characteristic nitroso- and acyl derivatives which they form with nitrous acid, acetic anhydride, etc.

The problem of ascertaining the constitution of the ψ-naphthoxazones has been greatly simplified by a consideration of the nature of the reactions employed in their synthesis. The occurrence of the pyridine ring in the molecule has been placed beyond doubt by the isolation of quinoline by the distillation of the unsubstituted ψ-naphthoxazone with zinc dust. The next question

of importance that has to be settled in order to arrive at a definite structure for each individual member of the series concerns the manner of attachment of the pyridine to the benzene nucleus. Thus, the reaction by which ψ-1:8-naphthoxazone is synthesised from 6-aminocoumarin may follow two different courses, according as the carbon atom adjacent to the amino-group taking part in the condensation occupies position 5 or 7 in the benzene ring. The compound in question may therefore be assigned either of the two following structures:

(I.)   (II.)
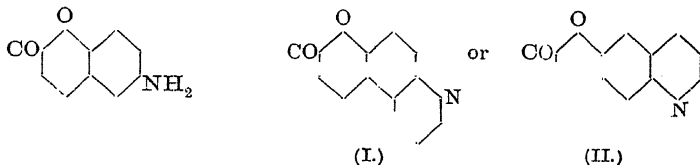
Although any direct evidence which might enable a decision to be made between these two possible constitutions is still lacking, the formula I appears to be the more plausible, and is also in harmony with certain general observations regarding the process of this condensation. Thus the substitution of a methyl group in position 7 does not hinder the progress of this reaction to the slightest extent, and this behaviour would be difficult to explain if it were assumed that the pyridine ring attached itself in the first place to the 7-carbon atom. The synthesis of alizarin-blue is another example of a similar nature where the condensation takes place smoothly with the *peri*-carbon atom corresponding with the 5-position in the coumarin ring.

The best solution of the problem appeared to lie in the synthesis of a ψ-naphthoxazone of structure II from 6-amino-7-methyl-coumarin and glyoxal, which, in the presence of alkalis, were expected to condense in the following manner (compare Kulisch, *Monatsh.*, 1895, **15**, 277):
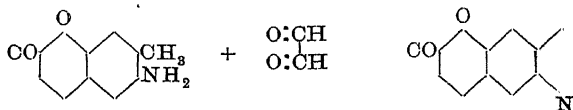
Attempts in this direction, however, have hitherto been unfruitful, and further experiments are in progress.

The determination of the structures of the ψ-benzo*iso*naphth-oxazones which have been obtained by analogous reactions from 6-nitro- and 6-amino-1:2-α-naphthapyrones does not present much difficulty, as in these cases only the carbon atom 5 is free to

participate in the reaction, which can therefore proceed only in the following way:

EXPERIMENTAL.

ψ-1:8-iso*Naphthoxazone*,
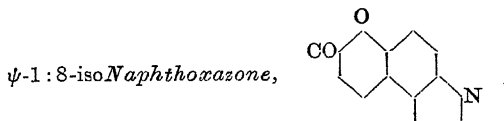
This substance was first prepared from 6-aminocoumarin by heating it with glycerol and sulphuric acid in the presence of 6-nitrocoumarin as the oxidising agent, according to the original directions of Skraup (*Monatsh.*, 1880, **1**, 316). The use of amino-coumarin was dispensed with later and the nitro-compound employed alone, the following conditions being found to give the most satisfactory results.

6-Nitrocoumarin (16 grams) and glycerol (19 c.c.) were mixed together, and concentrated sulphuric acid (17 grams) was gradually added, the mixture being cautiously heated in an oil-bath. A violent reaction set in at 145—150°, and as soon as this occurred the flask was removed from the bath and shaken vigorously. After the first reaction had subsided, the contents, which had now assumed a dark, tarry appearance, were again gradually heated to 160—170°, and maintained at this temperature for five to six hours. After cooling, the solid mass was broken up and repeatedly warmed with small amounts of water, and filtered until the filtrate ceased to exhibit a blue fluorescence. The latter, on keeping, deposited a small amount of crystals, which were found to be unchanged nitrocoumarin. This was removed and the acid filtrate rendered alkaline with dilute sodium hydroxide, care being taken to avoid an excess, as the freshly precipitated ψ-1:8-isonaphth-oxazone dissolves to a considerable extent in dilute alkali hydr-oxide even in the cold. The voluminous, pale yellow precipitate was collected, washed with cold water, and crystallised twice from boiling dilute alcohol with the aid of animal charcoal.

Thin, silky needles were deposited having a faint yellow colour and melting at 232° (uncorr.). The yield of the crystallised substance amounted to a little more than 6 grams, approximating to 40 per cent. of that required by theory:

0·0930 gave 0·2488 CO_2 and 0·0326 H_2O. $C = 72·9$; $H = 3·9$.

0·1333   ,,   8·3 c.c. N_2 at 30° and 745 mm. $N = 6·9$.

$C_{12}H_7O_2N$ requires $C = 73·1$; $H = 3·5$; $N = 7·1$ per cent.

The substance dissolves readily in alcohol, ether, chloroform, etc., to form colourless solutions, but its solutions in dilute sulphuric and hydrochloric acids exhibit a pale blue fluorescence, which is best seen on dilution. The crystallised substance is insoluble in dilute sodium hydroxide solution in the cold, but dissolves on boiling to give a deep yellow solution. The latter, on cooling and carefully neutralising with dilute sulphuric acid, slowly deposits the original material in a crystalline condition.

The *hydrochloride* is precipitated on passing dry hydrogen chloride into a solution of the substance in 90 per cent. alcohol. It forms a white, granular powder after being washed with absolute alcohol.

The *mercurichloride* crystallises from water in long, colourless, soft needles.

The *potassium mercuri-iodide*, which is first obtained as a curdy, white precipitate on adding Meyer's solution, very quickly changes into lustrous, leafy crystals.

The *picrate* is precipitated on mixing the constituents in hot benzene solution. It forms a yellow, crystalline powder melting at 212°.

The *platinichloride*, prepared by the usual method, crystallises in yellowish-brown needles:

0·0757 gave 0·0177 Pt. $Pt = 23·4$.

$(C_{12}H_7O_2N)_2, H_2PtCl_6, H_2O$ requires $Pt = 23·6$ per cent.

The *aurichloride* forms a bright yellow, crystalline precipitate, which rapidly turns brown in the air.

The *dichromate* crystallises in orange-red prisms, which are almost insoluble in water.

The *ferrocyanide* forms a shining, crystalline powder, which has a very characteristic colour resembling that of catechu. It dissolves in boiling water, the solution having an intense blue fluorescence. The ferrocyanide appears to be partly decomposed in the process of boiling its solution, as, on cooling the aqueous solution, the salt does not crystallise out, but a deep blue powder is gradually deposited along with clusters of small, colourless needles, which were identified as those of the original base.

A series of ammonium iodides has been obtained from ψ-1:8-*iso*-naphthoxazone by union with the alkyl iodides. These were prepared by the general method of heating the base with the alkyl iodide, with the addition of a little absolute alcohol, at 140° in sealed tubes. They possess a dark yellow to red colour, are fairly readily soluble in water, and crystallise on concentrating their aqueous solutions. The following have been prepared:

ψ-1 : 8-iso*Naphthoxazone* N-*methiodide* crystallises in thin, scarlet-red plates melting at 246°. The aqueous solution has a faint yellow colour:

0·1655 gave 0·1138 AgI.   I = 37·15.
$C_{13}H_{10}O_2NI$ requires I = 37·46 per cent.

It is practically insoluble in the ordinary organic solvents, such as benzene, ether, chloroform, etc., but readily dissolves in warm xylene to form a dark red solution with a fine violet fluorescence.

The N-*ethiodide*, $C_{14}H_{12}O_2NI$, forms orange-red crystals melting at 206°. Its solution in xylene has a reddish-violet colour and exhibits an intense pink fluorescence.

The N-n-*butyl iodide*, $C_{16}H_{16}O_2NI$, forms a dark yellow powder melting and decomposing at 209°. It agrees with the foregoing derivatives in its general behaviour.

The N-*amyl iodide*, $C_{17}H_{18}O_2NI$, melts and decomposes at 210°. It closely resembles the butyl derivative in its physical properties.

In order to examine the effect of the displacement of the alkyl groups by other complex groups on the colour of these substances, the following compounds were prepared, the first two of which were practically colourless, whilst the last had a pale yellow tint.

The N-*allyl bromide*, $C_{15}H_{12}O_2NBr$, forms small, white needles melting and decomposing at 320°.

The N-*benzyl chloride*, $C_{19}H_{14}O_2NCl$, crystallises from water in green needles melting at 265°.

The N-*phenylacetyl bromide*, $C_{20}H_{14}O_3NBr$, forms a pale yellow, crystalline powder melting and decomposing at 350°.

5 : 6 : 7 : 8-*Tetrahydro*-ψ-1 : 8-iso*naphthoxazone*.

ψ-1 : 8-isoNaphthoxazone (2 grams) was dissolved in concentrated hydrochloric acid (30 c.c.), granulated tin (5 grams) added, and the mixture gently boiled on a sand-bath under reflux for seven to eight hours. Next day water was added, and the tin was removed as sulphide. The filtrate was concentrated to about 100 c.c., and rendered alkaline with dilute ammonia; on cooling, the tetrahydro-derivative slowly separated in golden-yellow needles.

A single crystallisation from hot water, in which it was moderately soluble, rendered it quite pure, and the substance then melted sharply at 148°:

0·1624 gave 0·4257 CO_2 and 0·0818 H_2O. C=71·5; H=5·61.
0·1884 ,, 12·2 c.c. N_2 at 26° and 742 mm. N=7·3.
$C_{12}H_{11}O_2N$ requires C=71·64; H=5·47; N=7·00 per cent.

The N-*nitroso*-derivative, prepared in the usual manner, crystallised from alcohol in almost colourless needles melting at 175°:

0·1448 gave 15·15 c.c. N_2 at 22° and 757 mm. N=12·1.
$C_{12}H_{10}O_3N_2$ requires N=12·17 per cent.

The *benzoyl* derivative, $C_{19}H_{15}O_3N$, forms colourless plates, sparingly soluble in alcohol and melting at 252°.

9-*Methyl-ψ-1:8-isonaphthoxazone* was prepared from 6-nitro-7-methylcoumarin, the same precautions being taken as in the case of the preparation of the unsubstituted naphthoxazone. The product amounted to 3 grams from 8 grams of the nitro-derivative, the yield being approximately 35 per cent. of the theoretical. It crystallises in colourless needles melting at 200°:

0·1040 gave 6·4 c.c. N_2 at 30° and 744 mm. N=6·8.
$C_{13}H_9O_2N$ requires N=6·63 per cent.

The *picrate* crystallises in prismatic needles melting at 209°.
The *dichromate* crystallises from water in orange-yellow, flat prisms.
The *ferrocyanide* forms a chocolate-red, crystalline powder.
The *platinichloride* crystallises in deep yellow, small needles.
The *aurichloride* forms an amorphous, yellow precipitate.
The *mercurichloride* crystallises in soft, colourless, woolly needles.
The *potassium mercuri-iodide* forms clusters of pale yellow, prismatic needles.

5:6:7:8-*Tetrahydro-9-methyl-ψ-1:8-isonaphthoxazone*, prepared from the corresponding methylnaphthoxazone by reduction with tin and hydrochloric acid, crystallises in golden-yellow needles melting at 180°:

0·1650 gave 9·9 c.c. N_2 at 27° and 751 mm. N=6·75.
$C_{13}H_{13}O_2N$ requires N=6·51 per cent.

The *nitroso*-derivative, $C_{13}H_{12}O_3N_2$, forms a colourless, crystalline powder melting at 155°.

4:9-*Dimethyl-ψ-1:8-isonaphthoxazone* was obtained in a 20 per cent. yield by heating 6-nitro-4:7-dimethylcoumarin (m. p. 250°) with glycerol and sulphuric acid under the usual conditions. It crystallises from warm alcohol in silky needles melting at 238°:

0·1249 gave 7 c.c. N_2 at 27° and 748 mm. $N = 6·3$.

$C_{14}H_{11}O_2N$ requires $N = 6·20$ per cent.

The *picrate* crystallises in yellow needles melting at 197°.

The *dichromate* forms a dark red, crystalline powder.

The *ferrocyanide* forms intense red, small prisms decomposing above 300°.

The *methiodide*, $C_{15}H_{14}O_2NI$, crystallises from water in dark brown needles melting at 195°.

5 : 6 : 7 : 8-*Tetrahydro*-4 : 9-*dimethyl*-ψ-1 : 8-iso*naphthoxazone* crystallises from alcohol in bright yellow needles melting at 190°. It is practically insoluble in hot water :

0·1438 gave 7·8 c.c. N_2 at 26° and 748 mm. $N = 6·15$.

$C_{14}H_{15}O_2N$ requires $N = 6·10$ per cent.

The *nitroso*-derivative, $C_{14}H_{14}O_3N_2$, prepared by adding a very dilute solution of sodium nitrite to a solution of the base in dilute hydrochloric acid at 0°, forms a colourless powder melting at 161°.

ψ-*Benzo*-1 : 8-iso*naphthoxazone*,
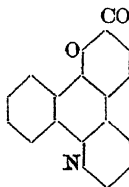
The starting point in the synthesis of this substance is 6-*nitro*-1 : 2-α-*naphthapyrone*, $C_{13}H_7O_4N$, which does not appear to have been described before. It was prepared by the ordinary process of nitrating 1 : 2-α-naphthapyrone dissolved in glacial acetic acid, adding concentrated sulphuric acid, and warming the mixture on the water-bath. It separates from hot glacial acetic acid in pale yellow nodules melting at 197°.

The assumption that the nitro-group enters position 6 is based on the fact that the 6-nitro-derivative is formed first in the nitration of 4-methyl-1 : 2-α-naphthapyrone (Dey, T., 1915, **107**, 1613).

ψ-*Benzo*-1 : 8-iso*naphthoxazone* crystallises in soft, pale yellow needles melting at 243°.   The yield amounted to 30 per cent. of the weight of the nitro-compound employed :

0·1490 gave 7·8 c.c. N_2 at 24·5° and 759 mm. $N = 5·9$.

$C_{16}H_9O_2N$ requires $N = 5·65$ per cent.

4-*Methyl*-ψ-*benzo*-1 : 8-iso*naphthoxazone*   was   prepared   from 6-nitro-4-methyl-1 : 2-α-naphthapyrone, and it exhibited the same

characteristics as the foregoing compound. The yield in one instance amounted to 50 per cent. of the theoretical.

It crystallises in pale yellow needles melting at 234°:

0·2291 gave 11·4 c.c. N_2 at 24° and 759 mm. $N = 5·6$.

$C_{17}H_{11}O_2N$ requires $N = 5·36$ per cent.

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XL.—*Mercury Mercaptide Nitrites and their Reaction with the Alkyl Iodides. Part V. Chain Compounds of Sulphur* (continued).

By SIR PRAFULLA CHANDRA RÂY and PRAFULLA CHANDRA GUHA.

THE present series of investigations has hitherto been confined to derivatives of monomercaptans; it has now been extended to those of the dimercaptans, of which 2 : 5-dithiol-1 : 3 : 4-thiodiazole may be taken as a typical representative.

When this dimercaptan is treated with mercuric nitrite, a dimercaptide dinitrite,

$$O_2NHgS \cdot C \colon N \cdot N \colon C \cdot SHgNO_2,$$
$$\underset{S}{\underline{\qquad\qquad}}$$
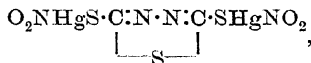
is not obtained, but the nitrous acid simultaneously disengaged oxidises the hydrogen atoms of two, three, four, and even six molecules of the dimercaptan, and the sulphur atoms become linked together and give rise to an interesting series of closed chain compounds. The maximum number of sulphur atoms forming the connecting link between two adjacent nuclei in the condensed complex molecule thus formed has so far been found to be twelve. Thus, in the case of a trinuclear condensation, we have

$$
\begin{aligned}
&\overset{*}{S} \cdot R'' \cdot S\,\text{H O H}\,S \cdot R'' \cdot S\,\text{H O H}\,S \cdot R'' \cdot S \\
&\quad\big|\qquad\qquad\qquad\qquad\qquad\quad\big| \quad = \\
&Hg\,|NO_2 \qquad\qquad\qquad\qquad O N O Hg
\end{aligned}
$$

$$
\begin{aligned}
&\quad S \cdot R'' \cdot S \cdot S \cdot R'' \cdot S \cdot S \cdot R'' \cdot S \\
&\quad\quad\big|\qquad\qquad\qquad\qquad\quad\big| \qquad + N_2O_3 + 2H_2O. \\
&\quad\quad Hg\text{————}O\text{————}Hg
\end{aligned}
$$
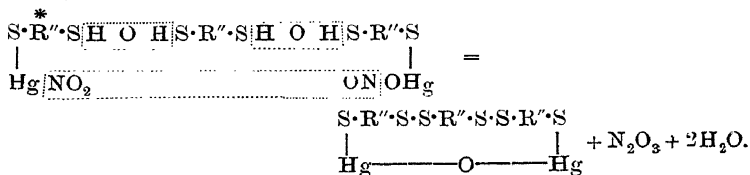
$$R''\ \text{denotes the bivalent group}\quad
\begin{array}{c}
\cdot C \colon N \cdot N \colon C \cdot \\
\big|\quad{}_{S}\quad\big|
\end{array}.$$

The heavy molecule of the dimercaptide dinitrite cannot retain the load of two NO_2 groups, and hence rupture takes place, as indicated by the dotted line, and a closed chain sulphoxy-derivative is finally formed with the liberation of nitrous fumes. The compounds thus generated are not, as a rule, nitrites. Some preparations, however, responded slightly to the nitrite tests, but the percentage of nitrogen due to the presence of nitrite was very low, proving that the proportion of the latter was insignificant. The occasional presence of some nitrite goes to establish the fact that the oxy-compound is in reality a decomposition product of the former.

If, instead of the dimercaptan itself, its potassium salt is used, the tendency towards oxidation by nitrous acid is excluded and a mercaptide nitrite of the formula

$$KS \cdot C \vdots N \cdot N \vdots C \cdot SHgNO_2$$
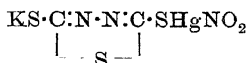
is obtained.

The sulphoxy-compounds may be represented by the general formula $(C_2N_2S_3)_x,Hg_2O$, where $x = 2$, 3, 4, or 6. A condensation product of five molecules has not yet been obtained. It is not easy to explain why in one operation the value of x should be two and in others it should rise to six; possibly the concentration of the parent substances is the main determining factor. It has often been found that two preparations under similar conditions had identical compositions. In the majority of cases, the value of x was found to be three, occasionally two and four, and only rarely six.

The preparations could not have been admixtures, because each of them strictly conformed to a definite formula. The most convincing proof of these compounds being of definite composition, however, is afforded by their reaction with the alkyl iodides. These sulphoxy-compounds behave exactly like mercaptide nitrites, and yield, as a rule, the corresponding sulphonium derivatives and, in a few cases, those with a less number of nuclei. The reducing action of the alkyl iodide removes the oxygen atom of the sulphoxy-ring, and, the bonds being thus snapped, an open-chain compound is formed, thus:

$$\begin{array}{c} S \cdot R'' \cdot S \cdot S \cdot R'' \cdot S \cdot S \cdot R'' \cdot S \\ | \qquad\qquad\qquad\qquad | \\ Hg\text{————}O\text{———}{-}Hg \end{array} \xrightarrow{\text{RI}} \quad IHgS \cdot R'' \cdot S \cdot S \cdot R'' \cdot S \cdot S \cdot R'' \cdot SHgI \,.$$
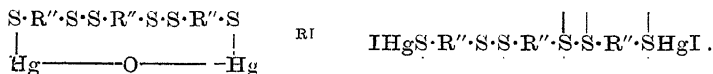
The six sulphur atoms of the chain now become quadrivalent by taking up the components of the alkyl iodide.

In this manner, a series of tetra-, hexa-, octa-, and dodeca-sulphonium compounds have been prepared. Each of these, with the exception of the propyl and butyl derivatives, is characterised by its crystalline character, and, moreover, its successive crops have the same melting point; the possibility of their being mixtures is thus precluded.

Another interesting point is the shifting of the double bonds, thus:

$$\begin{array}{cc} \text{N——N} & \text{N=\!=N} \\ \ddot{\text{C}}\quad\ddot{\text{C}}\cdot & \text{R}\!\!>\!\!\text{C}\quad\text{C}\!\!<\!\!\text{R} \\ \diagdown/ & \diagdown/ \\ \text{S} & \text{S} \end{array}$$

where R = methyl, ethyl, propyl, or butyl. As a rule, this is confined only to one nucleus. There is here evidently an extension of Thiele's theory to nitrogen compounds.

In one isolated instance, and that in the case of the reaction with methyl iodide, instead of there being a shifting of the double bonds, both the pairs of nitrogen and carbon atoms throughout the molecule were saturated by taking up additional methyl groups, thus:

$$\begin{array}{ccc} \text{N——N} & & \text{MeN——NMe} \\ \ddot{\text{C}}\quad\ddot{\text{C}}\cdot & {}_{+\text{Me}} & \text{Me}\!\!>\!\!\text{C}\quad\text{C}\!\!<\!\!\text{Me} \\ & & \diagdown/ \\ & & \text{S} \end{array}$$
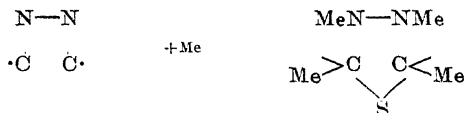
EXPERIMENTAL.

Sulphoxy-compounds.

General Method of Preparation.—2 : 5-Dithiol-1 : 3 : 4-thiodiazole, prepared according to Busch's method (*Ber.*, 1894, **27**, 2518), in dilute alcoholic solution, was added drop by drop with vigorous stirring to a solution of mercuric nitrite, care being taken that the latter was always in excess. In this manner, a semi-gelatinous, pale yellow precipitate was obtained, which was washed with water and dried in a vacuum desiccator. The powdered, granular mass was then heated under reflux successively with alcohol and benzene to remove any adhering accidental organic impurities, namely, the parent dimercaptan or its oxidation product, the disulphide. This precaution was, however, found to be unnecessary. The compounds obtained in this way are always associated with some molecules of water.

Potassium Salt of 2:5-*Dithiol*-1:3:4-*thiodiazole and Mercuric Nitrite.*

With an aqueous solution of the potassium salt, a compound of the formula

$$KS \cdot C\!:\!N \cdot N\!:\!C \cdot SHgNO_2$$
$$\underset{\displaystyle S}{\big|_____\big|}$$

with $12H_2O$ is obtained. Analysis of the substance gave:

Found: $Hg = 31 \cdot 50$; $S = 13 \cdot 89$; $C = 3 \cdot 53$; $H = 5 \cdot 34$.*
$C_2O_2N_3S_3HgK,12H_2O$ requires $Hg = 30 \cdot 81$; $S = 14 \cdot 79$; $C = 3 \cdot 70$; $H = 3 \cdot 70$ per cent.

2:5-*Dithiol*-1:3:4-*thiodiazole and Mercuric Nitrite: Formation of the Dinuclear Sulphoxy-compound,*

$$\begin{array}{c} S \cdot C_2N_2S \cdot S_2 \cdot C_2N_2S \cdot S \\ |\qquad\qquad\qquad\qquad\quad | \\ Hg\!-\!\!-\!\!-\!\!-\!O\!-\!\!-\!\!-\!\!-\!Hg \end{array}, 3H_2O.$$

Found: $Hg = 52 \cdot 57$, $52 \cdot 42$; $S = 23 \cdot 76$; $N = 7 \cdot 36$.
$C_4ON_4S_6Hg_2,3H_2O$ requires $Hg = 52 \cdot 22$; $S = 25 \cdot 07$; $N = 7 \cdot 31$ per cent.

Trinuclear Sulphoxy-compound,

$$\begin{array}{c} S \cdot C_2N_2S \cdot S_2 \cdot C_2N_2S \cdot S_2 \cdot C_2N_2S \cdot S \\ Hg\text{-}\qquad\qquad\text{---}O\text{-}\qquad\text{---}Hg \end{array}$$

In this case, each distinct preparation gave the compound associated with 8, 5, and 2 molecules of water respectively.

Compound with $8H_2O$.

Found: $Hg = 40 \cdot 21$; $S = 27 \cdot 56$; $C = 8 \cdot 50$; $N = 8 \cdot 18$.
$C_6ON_6S_9Hg_2,8H_2O$ requires $Hg = 39 \cdot 85$; $S = 28 \cdot 69$; $C = 7 \cdot 17$; $N = 8 \cdot 37$ per cent.

Compound with $5H_2O$.

Found: $Hg = 42 \cdot 07$; $S = 30 \cdot 21$; $N = 9 \cdot 36$.
$C_6ON_6S_9Hg_2,5H_2O$ requires $Hg = 42 \cdot 11$; $S = 30 \cdot 31$; $N = 8 \cdot 84$ per cent.

Compound with $2H_2O$.

Found: $Hg = 45 \cdot 33$; $S = 31 \cdot 40$; $N = 9 \cdot 52$.
$C_6ON_6S_9Hg_2,2H_2O$ requires $Hg = 44 \cdot 65$; $S = 32 \cdot 14$; $N = 9 \cdot 38$ per cent.

On repeating the preparation, the same trinuclear condensation

* The percentage of hydrogen is often too high as traces of mercury vapour are apt to be carried over to the calcium chloride tube; in many cases, therefore, the value of hydrogen has not been given.

product was obtained, although sometimes in an impure form. Thus in one preparation there was found $Hg = 42\cdot52$, $S = 34\cdot54$, and in another, $Hg = 43\cdot72$, $S = 31\cdot53$. However, on treating each of these with the alkyl iodides, the same sulphonium compound was obtained (see p. 546).

Tetranuclear Sulphoxy-compound, $(C_2N_2S_3)_4,Hg_2O$.

Compound with $3H_2O$.

Found: $Hg = 37\cdot94$; $S = 37\cdot54$; $N = 11\cdot48$.

$C_8ON_8S_{12}Hg_2,3H_2O$ requires $Hg = 37\cdot67$; $S = 36\cdot16$; $N = 10\cdot55$ per cent.

Compound with $5H_2O$.

Found: $Hg = 37\cdot21$; $S = 35\cdot13$; $N = 9\cdot55$.

$C_8ON_8S_{12}Hg_2,5H_2O$ requires $Hg = 36\cdot43$; $S = 34\cdot97$; $N = 10\cdot2$ per cent.

Hexanuclear Sulphoxy-compound, $(C_2N_2S_3)_6,Hg_2O,7H_2O$.

Found: $Hg = 28\cdot52$; $S = 39\cdot82$; $N = 11\cdot59$.

$C_{12}ON_{12}S_{18}Hg_2,7H_2O$ requires $Hg = 27\cdot97$; $S = 40\cdot28$; $N = 11\cdot75$ per cent.

Reaction with the Alkyl Iodides.

General Method of Preparation.—The above sulphoxy-derivatives were heated with the alkyl iodides on a water-bath under reflux for several hours, the product being allowed to remain overnight. Sometimes a crystalline mass, and occasionally a heavy, dark brown oil, settled at the bottom; the excess of alkyl iodide was decanted or distilled off, and the product dissolved in the minimum quantity of acetone and the solution filtered from the insoluble matter whenever necessary. On adding ether to the filtrate, a pale yellow, mealy, crystalline precipitate was obtained, and this process was repeated in order further to purify the substance.

Dinuclear Condensation.

The Compound, $C_4ON_4S_6Hg_2$, *and Methyl Iodide: Formation of the Compound,*
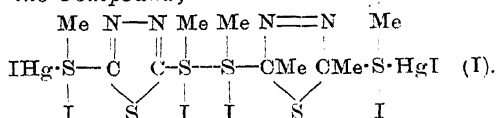
The product melted at 101—102°.

Found: $Hg = 25 \cdot 94$; $I = 49 \cdot 23$; $C = 7 \cdot 75$.
$C_{10}H_{18}N_4S_6Hg_2I_6$ requires $Hg = 25 \cdot 84$; $I = 49 \cdot 33$; $C = 7 \cdot 75$ per cent.

The corresponding *compound* with ethyl iodide (II) was sparingly soluble in acetone, and was therefore purified by crystallisation from the boiling solvent; it melted at $107°$.

Found: $Hg = 24 \cdot 19$, $24 \cdot 58$; $I = 43 \cdot 20^{*}$; $C = 11 \cdot 25$, $11 \cdot 42$; $N = 3 \cdot 53$.
$C_{16}H_{30}N_4S_6Hg_2I_6$ requires $Hg = 24 \cdot 51$; $I = 46 \cdot 69$; $C = 11 \cdot 76$; $N = 3 \cdot 43$
per cent.

The corresponding dinuclear tetrasulphonium compounds with n-propyl and n-butyl iodides did not crystallise, but consisted of dark brown, pasty masses, which were purified by repeated precipitation with ether from acetone solution.

Compound with n-*propyl iodide* (III).

Found: $Hg = 23 \cdot 89$; $I = 44 \cdot 74$; $C = 14 \cdot 05$.
$C_{22}H_{42}N_4S_6Hg_2I_6$ requires $Hg = 23 \cdot 31$; $I = 44 \cdot 40$; $C = 15 \cdot 38$ per cent.

Compound with n-*butyl iodide* (IV).

Found: $Hg = 21 \cdot 77$; $I = 41 \cdot 75$; $C = 17 \cdot 66$; $N = 3 \cdot 11$.
$C_{28}H_{54}N_4S_6Hg_2I_6$ requires $Hg = 22 \cdot 22$; $I = 42 \cdot 33$; $C = 18 \cdot 60$; $N = 3 \cdot 11$
per cent.

Trinuclear Condensation.

The Compound, $C_6ON_6S_9Hg_2$, *and Methyl Iodide: Formation of the Compound*,

Me N—N Me Me N—N Me Me N≡N   Me
IHg·S—C   C—S—S—C   C—S—S—   ·CMe CMe·S·HgI (V).
   I   S   I   I   S   I   S   I
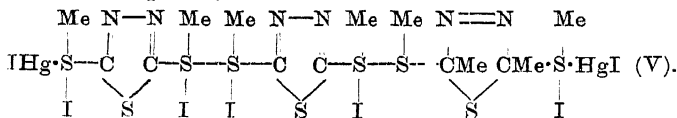
The product of the interaction was an oil. It was dissolved in hot acetone, and the solution, on cooling, deposited a crystalline mass, which when recrystallised from hot acetone yielded needle-shaped crystals melting at 101—$102°$, identical with the compound, $C_{10}H_{18}N_4S_6Hg_2I_6$, described above. The original mother liquor, on concentration, gave two successive crops melting at 85—$86°$.

Found: $Hg = 21 \cdot 55$; $C = 8 \cdot 66$.
$C_{14}H_{24}N_6S_9Hg_2I_8$ requires $Hg = 20 \cdot 20$; $C = 8 \cdot 48$ per cent.

* As a large quantity of copper powder has to be used and the process is a tedious one, the values for iodine and sulphur are sometimes too low (see T., 1916, **109**, 611).

Compound with Methyl Iodide in which all the Double Bonds are Saturated,

$$\text{Me} \quad \text{NMe—NMe} \quad \text{Me}$$

$$\cdot\text{S—CMe} \quad \text{CMe—S}\cdot \qquad Hg_2I_2 \ (VI).$$
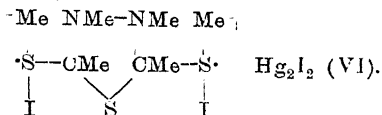
The method of preparation and purification was the same as in the case of the preceding compound. It is a white, crystalline substance melting at 94°.

Found: Hg = 18·24; S = 11·36; C = 13·15; H = 2·54.

$C_{24}H_{54}N_6S_9Hg_2I_8$ requires Hg = 18·78; S = 13·52; C = 13·52; H = 2·53 per cent.

The formation of this type of compound has been observed only in this one instance.

Compound with n-*Propyl Iodide* (VII).

This conforms to the ordinary type.

Found: Hg = 18·54; I = 44·61; C = 16·47.

$C_{30}H_{56}N_6S_9Hg_2I_8$ requires Hg = 18·14; I = 46·1; C = 16·33 per cent.

As will be noticed, the trinuclear sulphoxy-compound gives with methyl iodide compounds I and V, the latter being the chief product. This tendency towards the formation of the dinuclear tetrasulphonium compound from the higher nuclear sulphoxy-compounds is particularly noticeable in the case of the reaction with ethyl iodide, when only the dinuclear sulphonium compound (II) is obtained, even from tri- and tetra-nuclear sulphoxy-derivatives. In all these cases of formation of a lower member from the higher sulphoxy-compounds, a dark brown, pasty substance with a penetrating odour and lachrymatory properties was always produced, which resisted all attempts at purification.

Hexanuclear Condensation.

The Compound, $C_{12}ON_{12}S_{18}Hg_2$, *and Ethyl Iodide: Formation of the Compound,*

$$\text{Et} \quad \text{N—N} \quad \text{Et} \qquad \text{Et} \quad \text{N} \!=\! \text{N} \qquad \text{Et}$$

$$\text{IHg}\cdot \ \cdot\text{S—C} \quad \text{C—S}\cdot \quad \cdot\text{S—CEt} \quad \text{CEt·S·HgI} \ (VIII).$$
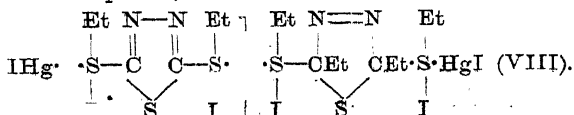
This melted at 90—91°.

Found: I = 50·03; N = 3·90; C = 13·14.

$C_{40}H_{70}N_{12}S_{18}Hg_2I_{14}$ requires I = 51·20; N = 4·84; C = 13·82 per cent.

It will thus be seen that the type persists throughout, in that the alteration in the position of the double bond is limited to only one nucleus of the chain.

In the previous communications, the compounds there described were tentatively classed under the sulphonium group, although no direct proof could be adduced in support of this view. One of the purest compounds of this series, namely, $MeEtS_2,HgI_2,EtI$ (T., 1916, **109**, 606), was selected for molecular weight determination in acetone solution by the ebullioscopic method; the value obtained was 712, that required by theory being 718. It is thus evident that the constitution is atomic (compare Hilditch and Smiles, T., 1907, **91**, 1396).

A study of the physical properties of the interesting poly-sulphonium compounds treated of in this paper is being undertaken which, it is hoped, will throw additional light on their constitution.

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XLI.—*Mercury Mercaptide Nitrites and their Reaction with the Alkyl Iodides. Part VI. Chain Compounds of Sulphur* (continued).

By SIR PRAFULLA CHANDRA RÂY.

THE present investigation deals with the chain compounds of sexa-valent sulphur. On treating the product of the interaction of thiocarbamide and mercuric nitrite, namely, the sulphoxynitrite,

$$NH_2 \cdot C(:NH) \cdot S(HgNO_2) {<}^{Hg}_{O}$$ (T., 1917, **111**, 102), with ethyl

iodide, a yellow, crystalline substance was obtained which was soluble in acetone, and, on purification by precipitation with ether, melted at 98—100°. Analysis proved it to conform to the formula $Et_2S_2,EtI,2HgI_2$; in other words, it is a member of the disulphonium series already described (T., 1916, **109**, 134) with an additional molecule of mercuric iodide in combination, to which should be assigned the constitutional formula

$$IHg \cdot SEt_2I_2 \cdot SEtI \cdot HgI,$$
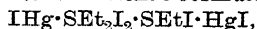
one of the sulphur atoms in the chain becoming sexavalent. The formation of this compound suggested the possibility of the direct conversion of all the members of the series $RR'S_2,R'I,HgI_2$ into $RR'S_2,R'I,2HgI_2$. This anticipation has been realised with one notable exception. When the alkyl group happens to be methyl, combination with an extra molecule of mercuric iodide does not take place. The presence of the radicle ethyl, on the other hand, favours the combination. Thus in the above series, where $R = Me$ and $R' = Pr^a$ or butyl, the extra valencies of the sulphur atom are not revived, but if R' happens to be ethyl, this anomaly disappears. To what extent the ethyl group favours the increase in valency will be evident from a typical case. When mercury ethylmercaptide nitrite, $EtS \cdot HgNO_2$, is treated with methyl iodide, by an interchange of the radicle, the compound, $EtMeS_2,HgI_2,MeI$, is obtained (T., 1916, **109**, 603); but in this case, although there are two methyl groups, the presence of a single ethyl group is sufficient to counteract the prejudicial influence of the former, and the compound, $EtMeS_2,MeI,2HgI_2$, is readily formed.

The marked genetic affinity of the radicle ethyl for sulphur and its influence on the increase in its valency is further evidenced by the fact that a compound of the empirical formula

$$Et_4S_2,2EtI,HgI_2$$
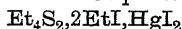
has also been obtained from ethyl sulphide by its reaction with ethyl iodide and mercuric iodide. On repeating Smiles's experiment (T., 1900, **77**, 161), under slightly altered conditions, with a view to ascertain the maximum valency of sulphur, it was noticed that whilst the main product was the compound, Et_3SI,HgI_2, as found by this author, there was always a considerable amount of a shining, crystalline substance, practically insoluble in cold acetone. As it had a sharp melting point when crystallised from hot acetone, it was analysed, with the result that the formula given above was established. What evidently happens is that under the joint action of mercuric iodide and ethyl iodide, or rather their ions, the bivalent sulphur atoms of two adjacent molecules of ethyl sulphide become sexavalent, with the formation of the compound, $SEt_3I_2 \cdot SEt_3I \cdot HgI$.

It is remarkable that if, in the above reaction, ethyl iodide is substituted by methyl, propyl, or butyl iodide, the product in each case is completely soluble in acetone and conforms to the general formula Et_2RSI,HgI_2, but no product of the fusion of two ethyl sulphide molecules is formed. The differential property of ethyl as compared with other alkyl radicles is thus brought into relief.

It was expected that the general method of the preparation of

the disulphonium compounds already described, namely, the treatment of ethyl mercurimercaptide nitrite, $EtS \cdot HgNO_2$, with ethyl iodide, should also yield the chain compound containing both the sulphur atoms in the sexavalent state. This expectation has also been realised. The latter compound is produced in such small amount that on previous occasions its formation was overlooked. It has already been shown that ethyl disulphide, ethyl iodide, and mercuric iodide also combine directly to yield the disulphonium compound, Et_2S_2,HgI_2,EtI (loc. cit.). Recently, this preparation has been repeated, and it has been found that the sexavalent disulphur compound is also formed in considerable quantity along with the former. It is thus evident that both the chain compounds, containing quadri- and sexa-valent sulphur respectively, are formed simultaneously.

It is of interest to note that Smiles and Hilditch, who treated an acetone solution of molecular proportions of ethyl disulphide and mercuric iodide with ethyl iodide, obtained diethylthioethylsulphonium dimercuric iodide, $(C_2H_5)_3S_2I,2HgI_2$ (T., 1907, **91**, 1396). It is evidently the same compound as has been described above.

An explanation may be offered as to why it is that in the first series of compounds only one of the two atoms of sulphur exists in the sexavalent condition; here the quadrivalent sulphur, being already weighted with the heavy load of the ions $HgI^{\cdot}$ and I', has lost the capacity of taking up an additional charge; in other words, of acquiring the maximum valency. In the solitary instance, however, in which both the sulphur atoms happen to be sexavalent, it will be noticed that there is only one set of $HgI^{\cdot}$ and I' ions; the sulphur atom combined with the latter has attached to it three additional comparatively light ethyl radicles, whereas the other sulphur atom, not having to bear the load of the heavy HgI-group, is in a position to take up three ethyl groups and two iodine atoms. Facts are already known which go to support the view that the maximum valency of an element is often conditional on the load of the radicles. The author hopes in a succeeding communication to show that platinum when attached to the radicle of 5-thiol-2-thio-3-phenyl-2:3-dihydro-1:3:4-thiodiazole, is in the tervalent condition. It is none the less inexplicable why the light radicle methyl should stand in the way of one of the atoms of sulphur attaining its maximum valency. The anomalous behaviour of the first member of the alkyl series is, however, well known.

Experimental.

The general method of preparation of the series $R_2S_2,RI,2HgI_2$ has already been incidentally described. These members are readily obtained by dissolving the corresponding disulphonium compound in acetone and adding mercuric iodide to the solution until no more is absorbed. The golden-yellow liquid is decanted from the undissolved iodide, and, on adding ether, a copious deposit of yellow, mealy crystals is obtained. Solution in acetone and precipitation by ether is repeated until the product gives a fairly sharp melting point. It has been found that in some instances, especially in the case of the methylsulphonium compound,

$$Me_2S_2,MeI,HgI_2,$$
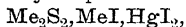
the acetone solution at first takes up a considerable quantity of mercuric iodide, but purification by the above process gradually removes all the mechanically held salt.

Compound $Et_2S_2,EtI,2HgI_2.$—(a) From the sulphoxynitrite derivative of thiocarbamide and ethyl iodide. The substance melted at 98°:

0·3656 gave 0·1250 Hg, 0·3540 AgI, and 0·1029 $BaSO_4$. Hg $= 34·19$; I $= 52·32$; S $= 3·87$.

0·2442 gave 0·0570 CO_2 and 0·0356 H_2O. C $= 6·37$; H $= 1·62$.

(b) By the direct union of mercuric iodide with the compound Et_2S_2,EtI,HgI_2. The substance melted at 100—101°:

0·2118 gave 0·0711 Hg. Hg $= 33·57$.

0·2118 ,, 0·0532 CO_2 and 0·0325 H_2O. C $= 6·85$; H $= 1·71$.

$C_6H_{15}I_5S_2Hg_2$ requires Hg $= 33·73$; I $= 53·54$; S $= 5·4$; C $= 6·07$; H $= 1·26$ per cent.

Compound $MeEtS_2,EtI,2HgI_2$ (m. p. 38—40°):

0·3840 gave 0·1236 Hg and 0·3768 AgI. Hg $= 32·19$; I $= 53·03$.

0·2094 ,, 0·0452 CO_2 and 0·0466 H_2O. C $= 5·87$; H $= 2·47$.

$C_5H_{13}I_5S_2Hg_2$ requires Hg $= 34·14$; I $= 54·19$; C $= 5·12$; H $= 1·11$ per cent.

Compound $MeEtS_2,MeI,2HgI_2$ (m. p. 50—55°):

0·2467 gave 0·2483 AgI and 0·0840 Hg. Hg $= 34·05$; I $= 54·39$.

0·1428 ,, 0·0286 CO_2 and 0·0211 H_2O. C $= 5·46$; H $= 1·64$.

$C_4H_{11}I_5S_2Hg_2$ requires Hg $= 34·55$; I $= 54·84$; C $= 4·14$; H $= 0·95$ per cent.

Compound $EtPr^aS_2,Pr^aI,2HgI_2+C_3H_6O$ (m. p. 30—31°).—This compound contains one molecular proportion of acetone:

0·4410 gave 0·1400 Hg.   Hg = 31·75.

0·1629   ,,   0·0586 CO_2 and 0·0352 H_2O.   C = 9·81; H = 2·40.

$C_8H_{19}I_5S_2Hg_2,C_3H_6O$ requires Hg = 31·45; C = 10·38; H = 1·97 per cent.

Compound $Et(C_4H_9)S_2,C_4H_9I,2HgI_2 + 1·5C_3H_6O$.—The substance had the consistency of treacle, and contained 1·5 molecular proportions of acetone:

0·3879 gave 0·1153 Hg and 0·3272 AgI.   Hg = 29·72; I = 45·58.

0·1340   ,,   0·0649 CO_2 and 0·0363 H_2O.   C = 13·21; H = 3·01.

$C_{10}H_{23}I_5S_2Hg_2,1·5C_3H_6O$ requires Hg = 30·10; I = 47·79; C = 13·10; H = 2·41 per cent.

Compound containing two sexavalent sulphur atoms (m. p. 146—147°). It was very sparingly soluble in cold acetone, but fairly readily so in the boiling solvent:

0·2991 gave 0·063 Hg and 0·2916 AgI.   Hg = 21·06; I = 52·69.

0·4032   ,,   0·8400 Hg and 0·2042 $BaSO_4$.   Hg = 20·86; S = 6·96.

0·1930   ,,   0·1068 CO_2 and 0·0538 H_2O.   C = 15·09; H = 3·09.

$C_{12}H_{30}I_4S_2Hg$ requires Hg = 21·14; I = 53·70; S = 6·77; C = 15·22; H = 3·17 per cent.

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XLII.—*Mercuric Sulphoxychloride.*

By SIR PRAFULLA CHANDRA RÂY and PRAFULLA KUMAR SEN.

THE close analogy between mercuric chloride and nitrite has been found to hold good throughout the investigations carried on from 1898 onwards. Thus, whilst mercuric nitrate with sodium sulphate at once gives an abundant yellow precipitate of the oxysulphate, the chloride and the nitrite fail to give it (T., 1897, **71**, 1103). The explanation lies in the fact that the latter salts are very feebly ionised in solution, and thus have no tendency to yield basic compounds. Ammonia, amines, and even a class of alkaloids have been found to behave towards mercuric nitrite in a manner similar to their action on the chloride (T., 1913, **103**, 3; 1917, **111**, 507).

The substituted thiocarbamides, thiocarbimides, thiobenzamide, etc., have been shown to give rise to a purely inorganic sulphoxynitrite of the empirical formula $[3(SHgNO_2),HgO]_2$, which is in

reality a chain compound containing six atoms of sulphur linked together (T., 1917, **111**, 104).

An attempt has been made to isolate the radicle $(SHgCl)_3$, which would be the analogue of mercuric iodosulphide, $(SHgI)_2$ *(loc. cit.,* p. 109), by treating mercuric chloride with some typical thio-compounds named above, as also thioacetic acid and ammonium dithiocarbamate. It was expected that in each case the radicle, SHgCl, would become detached from the parent substance and lead an independent existence. This expectation has been realised, but in a qualified sense. The radicle, SHgCl, no sooner separates out than it assumes the form $[3(SHgCl),HgO]_2$, which is the exact analogue of the oxynitrite. It has been shown already that the complex nitrite containing several nitro-groups, by the elimination of nitrogen trioxide, readily yields the oxynitrite.

It is not easy at first to understand how the chloride would also give rise to an oxy-salt. The explanation is obvious when it is considered that water takes part in the reaction; the compound $[3(SHgCl),HgO]_2$ is formed thus:

$$
\begin{array}{llll}
\text{HgCl} & \text{HgCl} \;\; \text{HgCl} & \text{HgCl} & \\
\quad | & \quad | \qquad | & \quad | & \\
\text{ClHg·S·S} & -\text{S}\!\!-\!\!-\!\!-\!\!\text{S}\!\!-\!\!-\!\! & -\text{S·S·HgCl} & = \\
\quad | & & & \\
\text{Hg|Cl H|O|H Cl|} & \text{Cl H|O H Cl|Hg} & &
\end{array}
$$

$$
\begin{array}{llll}
& \text{HgCl} \;\; \text{HgCl} \;\; \text{HgCl} & \text{HgCl} & \\
& \quad | \qquad | \qquad | & \quad | & \\
\text{ClHg·S·S}\!\!-\!\!-\!\!-\!\!\text{S}\!\!-\!\!-\!\!-\!\!\text{S}\!\!-\!\!- & & \text{S·S·HgCl} & + \; 4\text{HCl.} \\
& \quad | \qquad\quad\; | & & \\
& \;-\text{O} \qquad\; \text{O}- & -\text{Hg} &
\end{array}
$$
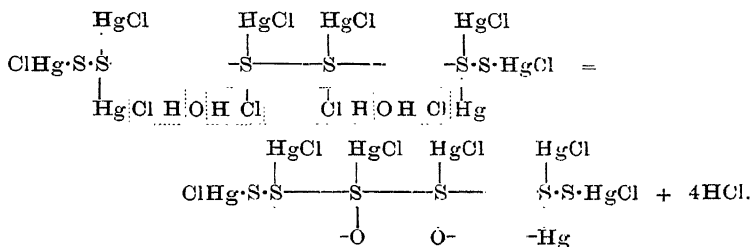
In other words, as soon as the radicle, SHgCl, is formed, three groups take up an additional molecule of mercuric chloride, that is, the radicles HgCl and Cl and a molecule of water simultaneously take part in the reaction, four molecules of hydrogen chloride are generated, and the oxygen atom forms the connecting link between the mercury atom, the neighbouring sulphur atom, and the two symmetrical complexes coalescing into a single molecule.

It is necessary to point out that whilst the radicle, $SHgNO_2$, has often a tendency to part company with the parent substance, the radicle, SHgCl, on the other hand, often remains attached to it. Thus thiocarbamide when acted on by mercuric chloride yields the compound $NH_2 \cdot C\!:\!NH \cdot SHgCl,HCl$, which is actually a hydrochloride, as will be shown in a subsequent communication. If, however, thiocarbamide is converted into its diacetyl derivative and then treated with mercuric chloride, the molecule is ruptured,

with the detachment of the radicle, SHgCl, and the formation of the oxychloride. *s*-Diphenylthiocarbamide also behaves similarly. Evidently the introduction of the negative radicles, acetyl and phenyl, neutralises the basic character of the compound due to the presence of an amino- and imino-group, and deprives it of the power of forming a hydrochloride, in which character alone it is stable.

It is a characteristic diagnostic property of mercaptans, real and potential, that with mercuric nitrite and chloride they yield the mercaptide nitrite and chloro-mercaptide respectively. Thioacetic acid, although an acid, contains the group SH and behaves like a typical mercaptan, thus :

$$CH_3 \cdot CO \cdot SH \xrightarrow{HgCl_2} CH_3 \cdot CO \cdot SHgCl.$$
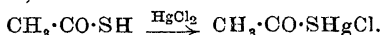
As soon as this compound is formed, it acts on a molecule of water, and the scission takes place as shown by the dotted line, a

$$CH_3 \cdot CO - | - SHgCl$$
$$H$$
$$OH$$
$$CH_3 \cdot CO - | - SHgCl$$
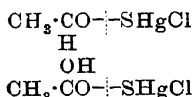
molecule of acetaldehyde and acetic acid being formed.

Ammonium dithiocarbamate assumes the tautomeric form, $SH \cdot C(:NH) \cdot SNH_4$, and both the radicles SH and SNH_4 with mercuric chloride yield SHgCl, which separates out.

Allylthiocarbimide, $C_3H_5 \cdot NCS$, combines with the elements of mercuric chloride, and the compound, $C_3H_5 \cdot N:C:SCl \cdot HgCl$, is temporarily formed, the sulphur atom becoming quadrivalent. As this configuration is unstable, a rupture takes place along the line of least resistance, the radicle, $:SCl \cdot HgCl$, decomposes into the stable radicle, SHgCl, and chlorine, whilst the organic portion of the complex, $R \cdot N:C:$, with a molecule of water yields a primary amine and carbon monoxide.

EXPERIMENTAL.

Method of Preparation.—The thio-compound in aqueous or alcoholic solution, as the case might be, was added in a thin stream by means of a pipette to an aqueous solution of mercuric chloride with vigorous stirring, care being taken that the latter ingredient was always in large excess.

A granular, white precipitate was obtained, which was washed first with water and then with alcohol, and finally dried in a vacuum over sulphuric acid. A special precaution is necessary in the case of allylthiocarbimide. If an alcoholic solution of it is

added to an aqueous solution of mercuric chloride, the white precipitate is obtained, but, at the same time, heavy, oily globules begin to settle down at the bottom, and it is not always easy to separate them from the sulphoxychloride. It is best to add the dilute alcoholic solution of the allylthiocarbimide to an alcoholic solution of mercuric chloride. The mixture remains clear, but on copious dilution with water and stirring, the white precipitate begins to appear. The mixture is allowed to remain overnight, and the product collected and treated as before.

The interaction of each of the above-mentioned thio-compounds and mercuric chloride was repeated several times, and the composition throughout was found to be identical. It is therefore not necessary to give the analysis of each preparation; that of one or two typical ones are given below.

Action of Mercuric Chloride on Diacetylthiocarbamide.

Diacetylthiocarbamide (Kohmann, *J. Amer. Chem. Soc.*, 1915, **37**, 2130) was dissolved in water and added drop by drop to a solution of mercuric chloride from a pipette with constant stirring. A white, amorphous precipitate was formed which, on remaining for twenty-four hours, became granular. It was collected, washed with water, and dried:

0·3276 gave 0·2591 Hg and 0·1354 AgCl.   Hg=79·1; Cl=10·2.
0·2419   ,,   0·1048 AgCl and 0·1647 $BaSO_4$.   Cl=10·7; S=9·4.
$[3(SHgCl),HgO]_2$ requires Hg=78·7; Cl=10·5; S=9·4 per cent.

The absence of carbon and hydrogen was confirmed by repeated combustion.

Action of Mercuric Chloride on s-Diphenylthiocarbamide.

The hot alcoholic solution of *s*-diphenylthiocarbamide was added to a solution of mercuric chloride, and the mixture was heated on a boiling-water bath under reflux for several hours. The white precipitate was collected, washed with hot alcohol and finally with water, and dried:

0·2591 gave 0·1097 AgCl and 0·1698 $BaSO_4$. Cl=10·47; S=9·0.
0·3684   ,,   0·2902 Hg.   Hg=78·8.

Mercuric Chloride and Thioacetic Acid.

Result of analysis:
0·2587 gave 0·2370 HgS.   Hg=79·0.
0·1465 ,,   0·0625 HgCl and 0·1070 $BaSO_4$.   Cl=10·55;
    S=10·0.

Mercuric Chloride and Allylthiocarbimide.

Result of analysis:

0·3402 gave 0·2631 Hg.   Hg = 77·34.

0·2795 ,, 0·1285 AgCl and 0·1818 $BaSO_4$.   Cl = 11·4; S = 8·9.

The absence of carbon was shown by combustion analysis.

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XLIII.—*The Preparation of Cadmium Suboxide.*

By HENRY GEORGE DENHAM.

VARIOUS suboxides of cadmium have long ago been described
(Tanatar, *Zeitsch. anorg. Chem.*, 1901, **27**, 433; Morse and Jones,
Amer. Chem. J., 1890, **12**, 488, etc.), although other investigators
have thrown doubt on the existence of these suboxides.   The
following experiments describe the efforts made to prepare a sub-
oxide of cadmium in as pure a state as has been the case with lead
suboxide.

Decomposition of Cadmium Oxalate.

The first method attempted was that described by Tanatar (*loc.
cit.*), namely, the decomposition of the oxalate in a stream of
carbon dioxide.   A sample of cadmium oxalate (Cd = 56·02 per
cent.) was heated at 300° in a rapid stream of carbon dioxide freed
from traces of oxygen by passage through heated copper.   At the
end of forty-eight hours the evolution of gas ceased, and examina-
tion revealed a small quantity of a green material, unmistakably
containing globules of cadmium, whilst the leading tubes were
lined with a deposit of the volatilised metal.   This experiment,
many times repeated, always gave the same result.

Precisely similar results were obtained when the carbon dioxide
was not employed, the evolved gases being removed by means of
a Sprengel pump.   Even when the total pressure of these gases
did not exceed 1 mm., the same green, heterogeneous substance was
produced.   Analysis of this material always gave values closely
approximating to Cd = 96·5 per cent. (Tanatar's Cd_4O contains
Cd = 96·56 per cent.).

Tanatar and Levin (*loc. cit.*) also describe how the oxide, Cd_2O, was obtained by the decomposition of a basic oxalate under similar conditions. A repetition of their experiment always gave a heterogeneous grey mass containing free cadmium.

An attempt was then made to remove by distillation the excess of metal present in the decomposition product of the oxalate. The mixture was heated to 350° without undergoing any change in appearance. The pump was then put into requisition, and in ten hours a large deposit of cadmium had volatilised out of the oven, whilst the residue was a homogeneous green mass, in which the microscope was no longer able to detect free metal. The following analytical results were obtained:

Oxalate. Grams.	Green substance. Gram.	$CdSO_4$. Gram.	Cd. per cent.
2·0	0·0362	0·0628	93·5
2·5	0·0592	0·1025	93·4
2·0	0·0809	0·1401	93·4

Cd_2O requires $Cd = 93·36$ per cent.

The method therefore appears to give a green oxide, but owing to the strong reducing action of the evolved carbon monoxide and the difficulty of distilling out the free metal, the method is not satisfactory.

Reduction by Hydrogen.

An attempt was made to prepare the suboxide by reducing the brown oxide with hydrogen (see Glaser, *Zeitsch. anorg. Chem.*, 1903, **36**, 1). At 240°, after twenty hours' reduction, the yellowish-green product appeared to be uniform, but the microscope clearly revealed globules of free metal. Reduction under varying conditions of temperature and pressure always led to this result. The excess of metal was afterwards removed by distillation, and a uniform, yellowish-green product obtained, in which the microscope revealed no sign of free metal. Analysis, however, showed that this substance was pure cadmium oxide (CdO), the colour change being either superficial or due to a different molecular aggregation.

Reduction by Carbon Monoxide.

It has been shown by Brislee (T., 1908, **93**, 162) that the time–reduction curve of cadmium oxide at 300°, with carbon monoxide as the reducing agent, shows a distinct break at a point which corresponds with the compound Cd_2O. Although it appeared

difficult to stop the reduction at the precise moment when the whole of the higher oxide had been reduced to the suboxide and none of the latter to the metal, it seemed feasible to carry through the reduction in such a way that the higher oxide was reduced to a mixture of the suboxide and metal, and this metal could then be removed by volatilisation.

An analysis of Brislee's time–reduction curve for 300° shows that the break occurs when the reduction has progressed for about twelve hours. An experiment was therefore carried out in which carbon monoxide was circulated for fourteen hours at 300° through two bulbs, each containing about 0·6 gram of cadmium oxide. One bulb was then sealed off, and the other heated in a vacuum for eighteen hours. The material in the first bulb was yellowish-green, containing visible globules of cadmium, whilst the second bulb gave a perfectly uniform, yellowish-green substance. Bulb I contained $Cd = 90·4$ and bulb II $Cd = 87·5$, whilst CdO requires $Cd = 87·57$ per cent. This experiment was repeatedly carried out at various temperatures between 300° and 310°, and in all cases the bulb sealed off before exhaustion contained a considerably higher percentage of cadmium than does CdO, approximating often to that of Cd_2O, but a moderately good pocket lens was sufficient in every case to show that the reduction product was heterogeneous and contained cadmium. Similarly, the bulb from which the excess of cadmium had been volatilised at the temperature of the experiment always gave a uniform, yellowish-green product exactly similar to that obtained when hydrogen was the reducing agent, and the composition of this was undoubtedly that of CdO. As a means of preparation of cadmium suboxide, this method therefore fails.

Morse and Jones's Method.

Morse and Jones (loc. cit.) have described how anhydrous cadmium chloride, when fused with cadmium, gives a product having the composition Cd_4Cl_7. This they consider to be possibly a mixture of $3CdCl_2 + CdCl$. On treatment with water, the product gave cadmous hydroxide, from which yellow cadmous oxide, Cd_2O, was readily obtained by dehydration. The author has repeated this work, and succeeded in reproducing the results described by Morse and Jones, but in spite of close attention to the details given in the original publication, he has never succeeded in converting more than 5 per cent. of the original chloride into suboxide, so that, as a practical method of preparing the suboxide in quantity, the method is not satisfactory.

In conclusion, it may be stated that the suboxide of cadmium may be obtained in small quantity by the method described by Morse and Jones, as well as by the decomposition of cadmium oxalate. The latter method, however, is only of use when the excess of metal, always formed during the decomposition, is distilled off in a vacuum, but the amount of residual cadmium suboxide is never more than 4 per cent. by weight of the original oxalate.

XLIV.—Formation of Diphenyl by the Action of Cupric Salts on Organometallic Compounds of Magnesium.

By JACOB KRIZEWSKY and EUSTACE EBENEZER TURNER.

A FEW years ago, it was shown (Bennett and Turner, T., 1914, **105**, 1057) that chromic chloride reacted quantitatively with magnesium phenyl bromide in the sense of the equation

$$2CrCl_3 + 2PhMgBr = 2CrCl_2 + 2ClMgBr + Ph \cdot Ph,$$
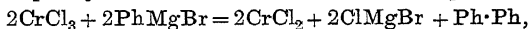
and the reaction was found to be a general one.

It has now been found that anhydrous cupric chloride behaves similarly to chromic chloride. Thus, when anhydrous cupric chloride is added to an ethereal solution of magnesium phenyl bromide, the following reaction occurs:

$$2CuCl_2 + 2PhMgBr = Cu_2Cl_2 + 2ClMgBr + Ph \cdot Ph,$$
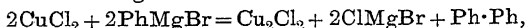
diphenyl being formed in almost the theoretical quantity. Furthermore, the preparation may be simplified, an equally good result being obtained by mixing, at the outset, magnesium turnings, ether, bromobenzene, and cupric chloride in the requisite proportions.

The anhydrous cupric chloride used was either the commercial preparation or that obtained by dehydrating the hydrated salt at 100°.

Anhydrous cupric sulphate reacts slowly with magnesium phenyl iodide, cupric iodide apparently being formed as an intermediate compound. It is hoped that this will ultimately lead to the preparation of cupric iodide. The reactions summed up by the equation

$$2CuSO_4 + 2PhMgI = Cu_2I_2 + 2MgSO_4 + Ph \cdot Ph,$$
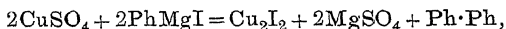
however, only proceed with difficulty, partly owing, no doubt, to the very sparing solubility of the anhydrous salt in ether.

In the presence of iodobenzene, a steady reaction occurs, probably according to the equations

$$PhMgI + PhI + CuSO_4 = MgSO_4 + CuI_2 + Ph \cdot Ph,$$
$$2CuI_2 + 2PhMgI = Cu_2I_2 + 2MgI_2 + Ph \cdot Ph.$$
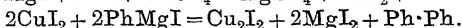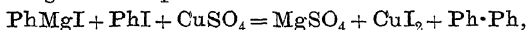
Thus when anhydrous cupric sulphate (1 mol.) is added to an ethereal solution of magnesium (2 atoms) and iodobenzene (3 mols.), a 65—70 per cent. yield of diphenyl is obtained.

Comparative experiments showed that the diphenyl produced was due neither to initial interaction of the magnesium and iodobenzene,

$$2PhI + Mg = MgI_2 + Ph \cdot Ph,$$
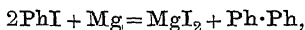
nor to interaction between magnesium phenyl iodide and iodobenzene,

$$PhMgI + PhI = MgI_2 + Ph \cdot Ph.$$
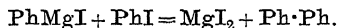
The reactivity of cupric sulphate with magnesium phenyl iodide seems to depend on the instability of the cupric iodide formed. Magnesium phenyl bromide does not react with cupric sulphate under similar conditions.

EXPERIMENTAL.

Action of Anhydrous Cupric Chloride on Magnesium Phenyl Bromide.

Magnesium turnings (4·9 grams) were covered with 150 c.c. of pure ether, 28 grams of anhydrous cupric chloride and then 32 grams of bromobenzene were added, and the mixture was well shaken. A vigorous reaction set in, and was controlled, when necessary, by shaking and external cooling. When the initial reaction had subsided, the mixture was heated under reflux in warm water for two hours, cooled, decomposed with ice and water, and treated with excess of concentrated hydrochloric acid in order to redissolve the precipitated cuprous chloride. The ethereal layer was separated, and the aqueous layer extracted repeatedly with ether. The united ethereal extracts were shaken with water to

precipitate the cuprous chloride remaining dissolved in the acidic ethereal solution, dried, and the solvent evaporated.   Thirteen grams (that is, about 85 per cent. of the theoretical) of pure diphenyl were obtained.

Using 100 c.c., and 55 c.c. of ether instead of the 150 c.c. used above, yields of 65 and 50 per cent., respectively, were obtained. An increase in the volume of ether to 200 c.c. was not found to be advantageous.

Interaction of Iodobenzene and Magnesium Phenyl Iodide.

Magnesium (4·9 grams), iodobenzene (41 grams), and ether (200 c.c.) were converted into the Grignard reagent, which was treated with 41 grams of iodobenzene, and the mixture heated under reflux for several hours. The product, on decomposition, gave 2·5 grams of diphenyl, half the iodobenzene used being recovered unchanged.

Interaction of Anhydrous Cupric Sulphate and Magnesium Phenyl Iodide.

Anhydrous cupric sulphate (32 grams) was added to the Grignard reagent, prepared from 41 grams of iodobenzene, 4·9 grams of magnesium, and 200 c.c. of ether, the mixture boiled for six hours under reflux, and then left overnight.   On working up the product, 6 grams of diphenyl were obtained, corresponding with a 39 per cent. yield on the iodobenzene used.

Interaction of Cupric Sulphate (1 mol.), Magnesium (2 atoms), and Iodobenzene (3 mols.) in Ethereal Solution.

Magnesium turnings (4·9 grams) were dissolved in 200 c.c. of pure ether in the presence of 62 grams of iodobenzene, and to the clear solution 16 grams of anhydrous cupric sulphate were added. The mixture was then boiled for three hours under reflux, cooled, decomposed with ice, and the solution obtained after acidifying extracted with ether,' and so on.   Sixteen grams of pure diphenyl were isolated, corresponding with a 66 per cent. yield on the iodobenzene used.

OBITUARY NOTICE.

EDWARD FRANK HARRISON.

BORN JULY, 1869; DIED NOVEMBER 4TH, 1917.

EDWARD FRANK HARRISON was educated at the United West-
minster Schools, and in 1884 was apprenticed to a pharmaceutical
chemist in North London. In 1890 he gained the Bell scholar-
ship of the Pharmaceutical Society, and proceeded to its school in
Bloomsbury Square. There he was awarded medals and certifi-
cates in chemistry, botany, and materia medica, and after passing
the minor and major examinations he occupied several positions
on the staff, and carried out research on the alkaloids of aconite.
While acting afterwards for five years with the firm of Messrs.
Brady and Martin at Newcastle, he successfully used his leisure
to prepare for the B.Sc. degree of London University. The next
six years were spent as head of the analytical department of
Messrs. Burroughs Wellcome and Co. In 1905 he went into
partnership in a school of pharmacy, but finally took up the in-
dependent practice of consulting and analytical chemistry. He
was an eminent specialist in the analysis of drugs and medicinal
substances, and as analyst to the British Medical Association made
nearly all the analyses of proprietary articles which were revealed
in the two publications "Secret Remedies" and "More Secret
Remedies."

In the Parliamentary inquiry which followed these disclosures,
Harrison was a most important witness and made a deep impression
on the Select Committee. The full value of this work to public
health and public economy has yet to be realised.

Col. Harrison was a Fellow of the Institute of Chemistry, and
published a number of papers on his special province of the science.
His process for estimating the diastatic strength of malts is now
in general use. He was active both as a student and a past student
in the life of the Pharmaceutical Society's School, in which he
was most highly regarded, and to which as his *alma mater* he was
loyally devoted. He was a member of the board of examiners,
and in 1917 he delivered a thoughtful and valuable address at
the inauguration of the session. For three years he conducted the
practical chemistry competitions maintained in the weekly

Pharmaceutical Journal. His professional life was, indeed, in the highest degree strenuous.

As soon as the War broke out Harrison was impatient to join the forces. After being refused several times on the ground of age, he became a special constable and a volunteer in the Inns of Court Reserve Corps. Later he succeeded in entering as a private in the Sportsmen's Battalion of the Royal Fusiliers. It was by an accident that he came under the notice of the first head of the anti-gas service at home, Col. Sir W. H. Horrocks, R.A.M.C., who with some difficulty succeeded in securing his services. He was given the rank of lieutenant on the general list in July, 1915, and from that time devoted himself to the anti-gas service. It was only in the last year that his duties extended over both branches of the gas service.

He was promoted major in April, 1916; lieut.-col. in January, 1917. He was appointed Assistant Controller of Chemical Warfare in November, 1917; shortly before his death, his succession to Major-General Thuillier as Controller of Chemical Warfare had been settled, and in a few days he would have attained the rank of brigadier-general.

Harrison's work for the war may be considered as falling into two periods. In the first period, extending from the spring of 1915 until November of 1916, he was engaged in research work in the anti-gas laboratories at the Royal Army Medical College, Millbank, the chief subjects being the improvement of the anti-gas helmet, the devising of, first, the large, and then the small box respirator.

In the early part of this period Harrison was constantly in the laboratory, working late into the night. He realised from the first the critical importance of speed and the possession of the initiative, and up to the last he never relaxed the pace. It is not easy to give an idea of the range of problems, their variety and complexity, that had to be overcome in bringing to a state of service efficiency such simple-looking appliances as the helmet and box respirator. The mechanical, chemical, physiological, and, one may add, even psychological questions raised were innumerable. Many heads and hands contributed to achieve the success that ensued. The apportionment of credit does not arise here, but there can be little doubt that all concerned would agree in giving Harrison a foremost place. With his scientific knowledge were united a strong practical instinct and intuitive judgment, which enabled him to seize quickly the essence of a problem and the substance of a suggestion, and to preserve a splendid sense of proportion. He improved the formula for the impregnating fluid

of the helmet, and worked out laboratory tests for controlling its component materials and for testing its efficiency. He made numerous experiments, in which he fearlessly wore the helmet in gases for which suitable quantitative control tests had not then been devised. During the late summer and autumn of 1915, he was occupied chiefly in getting out the large box respirator. As is generally known, this appliance was based on the admirable suggestion by Bertram Lambert, of Oxford, of a filter of permanganate—soda-lime granules. The realisation of this plan in the form of a box which in itself and its contents should be serviceable under field conditions was a most difficult undertaking. By the end of the year it was completed, and an issue was made early in 1916. The production in large quantities at a time when a high grade of protection was becoming indispensable for troops in special situations was a great achievement, and the large box was in its chief essentials the prototype of the small box which not long after became and remained the standard protection for troops of all arms. For the design of the small box, the members of the Gas Service in France were able to make valuable suggestions based on field experience with the large box. Harrison also made many contributions based on his own practical trials.

During the second period of his work, Harrison was closely associated with Col. Sir W. H. Horrocks in the rapid organisation and development of factories for the manufacture of respirators. Though this withdrew him for the greater part of his time from the laboratory, he remained in close touch with it, and at the weekly meeting of senior officers his genius for improvisation, his sound chemical judgment, and his foresight as to profitable lines of work were constantly evident. It was at this period that the manufacture of a new type of granule and of absorptive charcoal was worked out in the laboratories and transferred under the direction of selected officers to manufacturing establishments. In the choice of officers, Harrison's judgment rarely led him astray, and his knack of getting the right men into the right place contributed largely to the success of all his work. The great success of the small box respirator and its remarkable freedom from faults were due in no small measure to the organisation of inspecting officers, on which Harrison laid great stress. Harrison was held in high esteem by the officers of the Gas Services of our French, Italian, and American Allies. He was received with great cordiality at their councils, and his opinion was eagerly sought. It may be remarked, as affording a tribute to the excellence of the British respirator, that the Italians were supplied with several millions, and that the Americans, besides taking large numbers,

paid us the compliment of copying it as soon as the home manufacture could be arranged. The French considered that the protection it gave was even unnecessarily high.

In the last year of his life Harrison was called on to participate in the offensive side of gas warfare, and to exercise his great organising talent in what had become a very imposing and difficult undertaking. He had now reached the position to which his talents and labours so justly entitled him, but before he could actually officiate as Director of Chemical Warfare, the haunting fear of his friends was realised, and he was prostrated by influenza. His bodily strength, sapped by unceasing labour, was unequal to the strain, pneumonia supervened, and he passed away, as certainly as anyone on the battlefield, a sacrifice of the war. His elder son had fallen in France in 1916.

It is not easy to do justice to Harrison's personal qualities. He was a man of the strongest character. The love of his country, its ideals of freedom, its democratic institutions, and his belief in the destiny of the British as leaders among free peoples were the inspiration of his life and work. He had no thought for himself when the lives of others were at stake. The inflexible sense of duty which animated him communicated itself to those who worked with him, and he gained in a remarkable degree their respect and affection. He faced all emergencies with imperturbability, was never daunted or discouraged, and preserved a clear head and a power of decision even when worn out with incessant labour. He was neither dogmatic nor impatient, but always ready to improve on himself, listening with patience and courtesy to all honest criticism or advice. He was a master organiser, and the War brought him his opportunity. He died acknowledged and revered as a leader of men, his great task accomplished. He was buried with full military honours, mourned by a multitude of fellow-labourers who had learned something of his worth.

Harrison died before he had received the public honours that would undoubtedly have been conferred on him. He had been made C.M.G. in 1917, and the French had shown their appreciation of his services by making him Officer of the Legion of Honour. It is gratifying to know that a memorial to perpetuate his name is to be associated with the Chemical Society. What the nation owes him for the saving of life and the mitigation of suffering can scarcely be overestimated.

A. S.
H. S. R.

XLV.—*Studies on the Dependence of Optical Rotatory Power on Chemical Constitution. Part I. Position—Isomerism and Optical Activity of Naphthyliminocamphors and Derivatives of Phenyliminocamphor.*

By Bawa Kartar Singh and Jatindra Kumar Mazumder.

The relation between chemical constitution and rotatory power which is investigated in the present paper is that of position-isomerism in the aromatic groups present in optically active derivatives of phenyliminocamphor.

Frankland in 1896 (T., **69**, 1583) suggested a theory to explain the changes in rotatory power produced by nuclear substitution in the ortho-, meta-, and para-position in a side-chain containing an active group.

Taking the analogy of a weight acting at the end of a lever arm, he suggested, for reasons based on the relative position of the centre of gravity of the unsubstituted aromatic nucleus on the one hand, and those of the isomeric disubstituted derivatives on the other, that the order of rotatory power should be:

Ortho < unsubstituted nucleus < meta < para.

The line of argument adopted was as follows:

The centre of gravity of the unsubstituted nucleus being at the centre of a regular hexagon, that in the ortho-substituted derivative would be somewhat nearer, in the meta-derivative somewhat further, and in the para-derivative still further than that geometrical centre from the side-chain containing the optically active group.

If, then, the optical activity is determined by the moment of the mass of the group, the rotatory power of the para-compound should be the greatest, that of the ortho-compound the least, and that of the meta-derivative intermediate between those of the other two. In the case of the unsubstituted nucleus, the mass is smaller, but it acts through a longer arm than in the case of the larger mass of the ortho-compound, but through a shorter arm than in either the meta- or the para-compound.

In his Presidential Address to the Chemical Society (T., 1912, **101**, 654), Frankland revived this theory, and illustrated its validity by several observations of Cohen and his collaborators. A number of other observations (Cohen, T., 1903, **83**, 1214;

T., 1904, **85**, 1271; T., 1905, **87**, 1190; T., 1911, **99**, 1058), how-
ever, do not support the rule.

The aim of the present work is to afford evidence in support or
in refutation of Frankland's rule from observations made in
several series of new compounds. If the theory were correct, that
is, if the rotatory power were determined by the position of the
centre of gravity of the nucleus in relation to the active group, we
should expect: (1) that the greater the mass of the substituting
group or element, the greater would be the observed differences
between the constants of the para- and ortho-isomerides, and (2)
that the para-isomeride would have the maximum rotation.

The molecular rotatory powers of derivatives of phenylimino-
camphor are tabulated below.

TABLE I.

Derivatives of phenyliminocamphor.	$[M]_D$ in chloroform solution.			
	$-CH_3(15)$	$-Br(80)$	$-Cl(35\cdot5)$	$-O\cdot CH_3(31)$
Ortho-	$+1183°$	$+1382°$	$+441\cdot7°$	$+612°$
Meta-	1665	1338	1338	—
Para-	2177	1695	1768 (a)	3314 (a)

The value of $[M]_D$ of phenyliminocamphor is 1750° (Forster and
Thornley, T., 1909, **95**, 944).

TABLE II.

Derivatives of phenylimino-camphor.	$[M]_D$ in methyl alcohol.		
	$-CH_3(15)$	$-Br(80)$	$-Cl(35\cdot5)$
Ortho-	$+1030°$	$+1311°$	$+486\cdot4°$
Meta-	1504	1260	1261
Para-	2001	1545	

The value of $[M]_D$ for phenyliminocamphor in methyl alcohol
solution is 1462°.

The mean temperature of observations recorded in tables I and
II was 26° to 32°.

It will now be seen that in no case is Frankland's rule borne
out by the results recorded in tables I and II. In the case of the
tolyl and chlorophenyl derivatives, the value of the rotatory power
for the unsubstituted compound (namely, phenyliminocamphor)
lies between that for the meta- and para-derivative, and is there-
fore in opposition to Frankland's rule. The order of rotatory
powers in the case of the bromophenyl derivatives in chloroform
is meta < ortho < para < unsubstituted compound, and here
deviation from Frankland's rule is seen to be most marked.

Although the mass of the group (CH$_3$) in the case of the tolyl compounds is less than that in the case of the bromophenyl derivatives (Br), the observed difference in the values of the rotatory powers of the ortho- and para-isomerides is more than three times as high in the former as in the case of the latter. This result is again contrary to what we should expect if Frankland's rule were valid.

The para-isomeride has in all the above cases, except in the case of the bromophenyl derivative, the maximum rotation, and this is in accordance with the deduction made from Frankland's rule.

It is thus clear that the results recorded in the present paper do not generally support Frankland's rule. Only in one direction can we say that Frankland's theory has been supported, namely, that the ortho-compound has the least and the para-derivative the maximum rotation (except in one instance).

Cohen, as the result of his observations (T., 1910, **97**, 1737; 1911, **99**, 1060), lays down the following rule: The rotatory effect of the ortho-grouping differs more from that of the phenyl than do those of meta- and para-groupings. A glance at tables I and II will show that this rule is also not supported. In the case of the bromophenyl derivatives, it is the meta, and in the case of the methoxyphenyl derivatives it is the para, and not the ortho, which differs more in rotation from the value of the unsubstituted compound.

Further, no simple connexion can be observed between the nature of the substituting element or group in an optically active compound and its rotatory power. In the case of ortho-compounds (table I), it is seen that the order of elements or groups with increasing rotation is $Cl < O \cdot CH_3 < CH_3 < Br < H$, in the case of meta-compounds $Cl = Br < CH_3 < H$, and in the case of para-compounds $Br < H < Cl < CH_3 < O \cdot CH_3$.

Experimental.

o-*Tolyliminocamphor*, $C_8H_{14} {<}{\,}^{C:N \cdot C_6H_4 \cdot CH_3}_{CO}$.
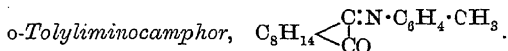
Camphorquinone and o-toluidine in molecular proportion were heated with anhydrous sodium sulphate for several hours on the water-bath. On cooling, water was added, when a solid substance was precipitated, which crystallised from 50 per cent. alcohol in yellow prisms melting at 120—121°.

It is very readily soluble in chloroform, ether, benzene, or acetone, less so in methyl or ethyl alcohol, and insoluble in water:

0.2074 gave 10·6 c.c. N$_2$ at 30° and 759·5 mm.   N = 5·78.

C$_{17}$H$_{21}$ON requires N = 5·49 per cent.

The following determinations of rotatory power were made by dissolving the given weight of substance in 19·9 c.c. of the solvent, and the first observation was made within half an hour of making up the solution.   This applies to all the observations, unless the contrary is stated.   The length of the tube was 2-dcm.

Solvent.	Substance. Gram.	Temperature.	Time hours.		$[\alpha]_D$.	$[M]_D$.
Chloroform	0.1470	32°	—	+6·85°	+464·1°	+1183°
			19	6·86	464·4	1184
Methyl alcohol......	0.1519	34	—	6·16	403·6	1030
			21	6·08	398·4	1016

m-*Tolyliminocamphor.*

Molecular proportions of camphorquinone and *m*-toluidine, mixed with a little fused sodium sulphate, were heated on the water-bath for five hours.   The product was cooled and dissolved in a small quantity of alcohol; water was added, when an oil separated which solidified on keeping.   The substance was crystallised from dilute (50 per cent.) alcohol in yellow prisms melting at 85—86°.

It is very readily soluble in methyl or ethyl alcohol, chloroform, ether, or acetic acid, and insoluble in water:

0·1425 gave 7·6 c.c. N$_2$ at 31° and 760 mm.   N = 5·9.

C$_{17}$H$_{21}$ON requires N = 5·49 per cent.

The rotatory power determinations gave the following values:

	Solvent.	Substance. Gram.	Temperature.	Time in hours.	a_D.	$[\alpha]_D$.	$[M]_D$.
(a)	Chloroform ...	0.0649	31°	—	+4·26°	+653·0°	+1665
	,, ...	,,	29·5	20	4·31	660·7	1684
(b)	,, ...	0.0915	17—18	—	6·04	656·7	1675
	Methyl alcohol	0.0903	31·0	—	5·35	589·7	1504
	,,	,,	29·5	13½	5·35	589·7	1504

p-*Tolyliminocamphor.*

An alcoholic solution of camphorquinone was mixed with a similar solution of *p*-toluidine (in molecular proportion), a little anhydrous sodium sulphate added, and the solution was heated on the water-bath under reflux for three hours.   After evaporating off the alcohol, the residue was poured into water, when a yellow substance separated, which crystallised from dilute alcohol (50 per cent.) in yellow prisms melting at 121—122°.   It is very readily soluble in chloroform, acetone, ether, or benzene, less so in methyl or ethyl alcohol, and insoluble in water:

0.2118 gave 10·6 c.c. N_2 at 29° and 764 mm.   N = 5·71.

$\quad\quad$ $C_{17}H_{21}ON$ requires N = 5·49 per cent.

The rotatory power determinations gave the following values :

Solvent.	Substance. Gram.	Temperature.	Time in hours.	a_D.	$[a]_D$.	$[M]_D$.
Chloroform ..	0·1691	28·0°		+14·51°	+853·9°	+2177°
Methyl alcohol	0·1583	29·0		12·48	784·5	2001
		29·0	48	11·95	694·5	1771
		30·5	76	10·2	641·1	1634·8
		29·5	142	8·79	552·6	1409
		30·5	166	8·26	519·2	1324
		30·0	219	7·55	474·5	1210

The substance when recovered from the polarimeter tube by evaporation to dryness on the water-bath melts at about 110°.

$$o\text{-}Bromophenyliminocamphor, \quad C_8H_{14}{<}{\overset{C\!:\!N\cdot C_6H_4Br}{CO}}$$
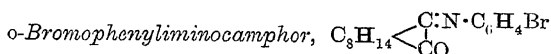
Camphorquinone was added to the calculated quantity of o-bromoaniline and a little anhydrous sodium sulphate, the mixture being heated on the water-bath for five hours, cooled, and then dissolved in alcohol. The alcoholic solution on dilution with water furnished an oil, which became solid on keeping for two or three days, and crystallised from dilute alcohol (50 per cent.) in yellow needles melting at 110°.

It is very readily soluble in methyl or ethyl alcohol, chloroform, ether, or acetic acid, and insoluble in water :

C 1109 gave 4·6 c.c. N_2 at 33° and 761 mm.   N = 4·65.

$\quad\quad$ $C_{16}H_{18}ONBr$ requires N = 4·4 per cent.

The rotatory power determinations gave the following values :

Solvent.	Substance. Gram.	Temperature.	Time in hours.	a_D.	$[a]_D$.	$[M]_D$.
Chloroform	0·0380	32·0°	—	+1·65°	+432·1°	+1382
,, ...	,,	31·0	14½	1·64	429·4	1374
Methyl alcohol......	0·0362	31·0	—	1·49	409·6	1311
,, ...	,,	31·5	20½	1·19	327·2	1047

m-*Bromophenyliminocamphor.*

Camphorquinone and m-bromoaniline were heated together in the presence of a little anhydrous sodium sulphate on the water-bath for four hours.   On cooling, the product was dissolved in alcohol and precipitated by the addition of water.   It crystallised from dilute alcohol (50 per cent.) in yellow prisms melting at 116—118°, which were very readily soluble in methyl or ethyl alcohol, chloroform, ether, or acetic acid, and insoluble in water :

0·1085 gave 0·0638 AgBr.   Br = 25·0.

$C_{16}H_{18}ONBr$ requires Br = 25·0 per cent.

The rotatory power determinations gave the following values:

Solvent.	Substance. Gram.	Temperature.	Time in hours.	α_D.	$[\alpha]_D$.	$[M]_D$.
Chloroform	0·1392	31°		+5·85°	+418·3?	+1338°
		31	7½	5·81	415·5	1329
Methyl alcohol......	0·1461	31		5·78	393·9	1260
		31	5	5·52	376·2	1204
		31	22	4·94	336·7	1077

The substance when recovered from methyl-alcoholic solution after the last observation by evaporating to dryness on the water-bath melted at 113—114°. A mixture with the original substance melted at 116—118°. It is therefore obvious that the substance undergoes mutarotation in methyl-alcoholic solution, and not in chloroform solution.

p-*Bromophenyliminocamphor*.

Camphorquinone and *p*-bromoaniline were mixed together in equal quantities. The reaction began at the ordinary temperature, as the mixture became liquid within a short time. After heating for four hours on the water-bath, the reaction was complete. On cooling, the product solidified, and crystallised from dilute alcohol (50 per cent.) in yellow needles melting at 138—139°. The substance is very readily soluble in methyl or ethyl alcohol, chloroform, ether, or acetic acid, and insoluble in water:

0·0750 gave 3·2 c.c. N_2 at 35° and 759 mm.   N = 4·74.

$C_{16}H_{18}ONBr$ requires N = 4·4 per cent.

The rotatory power determinations gave the following values:

Solvent.	Substance. Gram.	Temperature.	Time in hours.	α_D.	$[\alpha]_D$.	$[M]_D$.
Chloroform	0·1217	31°	—	+6·48°	+529·9°	+1695
,, ...		30	20	6·53	534·0	1709
Methyl alcohol...	0·1193	31	—	5·79	483·0	1545
,, ...	,,	30	22	4·31	359·5	1150
.. ...	..	30	46	3·36	280·2	896

The substance when recovered from methyl-alcoholic solution after the last observation, by evaporation to dryness, melted at 112—118°, a mixture with the original substance melting at 115—122°. It is clear that the substance exhibits mutarotation in methyl alcohol, but not in chloroform.

o-*Chlorophenyliminocamphor*, $C_8H_{14} < \begin{matrix} C{:}N{\cdot}C_6H_4Cl \\ CO \end{matrix}$.
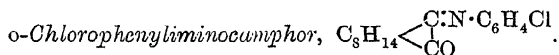
Camphorquinone and o-chloroaniline were condensed with the aid of a little sodium sulphate by heating on the water-bath for five hours. On allowing to cool, the substance solidified, and crystallised from dilute alcohol (50 per cent.) in silky, yellow needles melting at 128°.

It is very readily soluble in methyl or ethyl alcohol, chloroform, ether, or acetic acid, but sparingly so in water:

0·1233 gave 5·6 c.c. N_2 at 28° and 758 mm. N = 5·16.

$C_{16}H_{18}ONCl$ requires N = 5·1 per cent.

The rotatory power determinations gave the following values:

	Solvent.	Substance. Gram.	Temperature.	Time in hours.	a_D.	$[a]_D$.	$[M]_D$.
(a)	Chloroform ...	0·0633	27·5°	—	+1·02°	+160·4°	+441·7
	,, ...	,,	28·0	8	1·03	161·9	446·0
(b)	,, ...	0·0994	30·0	—	1·54	154·1	424·6
		(2nd prepn.)					
	,, ...	,,	31·0	7½	1·54	154·1	424·6
	Methyl alcohol	0·0941	30·0	—	1·67	176·6	486·4
	,,	,,	31·0	6½	1·67	176·6	486·6

m-*Chlorophenyliminocamphor*.

Molecular proportions of camphorquinone and m-chloroaniline were condensed with the aid of anhydrous sodium sulphate by heating on the water-bath for four hours. The product was cooled, dissolved in alcohol, and precipitated by the addition of water as a crystalline substance. On recrystallisation from dilute alcohol, pale yellow needles melting at 123—124° were obtained. The substance is very readily soluble in methyl or ethyl alcohol, chloroform, ether, or acetic acid, and insoluble in water:

0·1300 gave 6·2 c.c. N_2 at 32° and 758 mm. N = 5·35.

$C_{16}H_{18}ONCl$ requires N = 5·1 per cent.

The rotatory power determinations gave the following values:

Solvent.	Substance. Gram.	Temperature.	Time in hours.	a_D.	$[a]_D$.	$[M]_D$.
Chloroform	0·0666	28·0°	—	+3·25°	+485·7°	+1338°
	,,	27·5	24	3·19	476·7	1313
Methyl alcohol......	0·0800	27·5	—	3·68	457·7	1261
	,,	26·5	20	3·69	459·0	1264

$$\textit{a-Naphthyliminocamphor,}\ \ C_8H_{14}{<}{\overset{\text{C:N}\cdot C_{10}H_7}{\underset{\text{CO}}{|}}}.$$
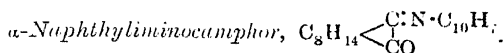
When molecular proportions of camphorquinone and α-naphthyl-amine were mixed, the mixture soon became liquid at the ordinary temperature.   It was heated on the water-bath for four hours to complete the reaction.   On cooling, the product was dissolved in alcohol and precipitated by the addition of water, when a solid substance separated which crystallised from dilute alcohol in yellow needles melting at 155°.

It is very readily soluble in methyl or ethyl alcohol, chloroform, ether, or acetic acid, and insoluble in water:

0·1220 gave 5·1 c.c. N_2 at 33° and 759 mm.   N = 4·7.

$C_{20}H_{21}ON$ requires N = 4·8 per cent.

The rotatory power determinations gave the following values:

Solvent.	Substance. Gram.	Tem-perature.	Time in hours.	a_D.	$[a]_D$.	$[M]_D$.
Chloroform	0·0676	31·5°		+4·14°	+609·6°	+1774°
„	„	32·0	9½	4·14	609·6	1774
Methyl alcohol......	0·1199	31·5	—	6·73	558·5	1625
		32·0	7½	6·73	558·5	1625

The substance does not exhibit any mutarotation.

β-Naphthyliminocamphor.

Camphorquinone and β-naphthylamine were condensed in mole-cular proportions by heating on the water-bath for four hours. The substance on crystallisation from dilute alcohol in the usual manner gave yellow needles melting at 140—142°.

These are very readily soluble in methyl or ethyl alcohol, acetic acid, ether, or chloroform, and insoluble in water:

0·1100 gave 4·6 c.c. N_2 at 32° and 760 mm.   N = 4·4.

$C_{20}H_{21}ON$ requires N = 4·8 per cent.

The rotatory power determinations gave the following values:

Solvent.	Substance. Gram.	Tem-perature.	Time in hours.	a_D.	$[a]_D$.	$[M]_D$.
Chloroform	0·0966	32°	—	+6·62°	+682·0	+1985°
		31	15	6·66	686·0	1996
Methyl alcohol......	0·1140	31		7·45	650·5	1893
		31	10½	7·35	641·6	1867

Phenyliminocamphor.

This substance was prepared according to Forster's method (T., 1909, **95**, 949), and formed silky, yellow needles melting at 110—112°.

z ✱

The rotatory power determinations gave the following values :

Solvent.	Substance. Gram.	Temperature.	Time in hours.	α_D.	$[\alpha]_D$.	$[M]_D$.
Methyl alcohol......	0·0920	26·5°	—	+5·61°	+606·8°	+1462°
,, ...	,,	27·0	27	5·51	596·1	1437

p-*Benzeneazophenyliminocamphor*, $C_8H_{14} < {C:N \cdot C_6H_4 \cdot N:N \cdot C_6H_5 \atop CO}$.
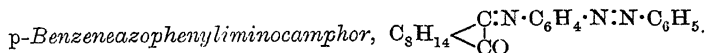
Camphorquinone and aminoazobenzene, in molecular proportions, were heated on the water-bath for six hours. The product was cooled, dissolved in alcohol, and precipitated as an oil by the addition of water. The oil, on keeping for two days, solidified. It crystallised from dilute alcohol in orange needles melting and decomposing at 129—130°.

The substance is very readily soluble in methyl or ethyl alcohol, chloroform, ether, or acetic acid, and insoluble in water :

0·1140 gave 12·5 c.c. N_2 at 32° and 759 mm.   N = 12·5.
    $C_{22}H_{23}ON_3$ requires N = 12·36 per cent.

The rotatory power determinations gave the following values :

Solvent.	Substance. Gram.	Temperature.	Time in hours.	α_D.	$[\alpha]_D$.	$[M]_D$.
Chloroform	0·0557	23·0°	—	+3·08°	+550·4°	+1899
,, ...	,,	23·5	22	3·25	580·8	2004
Methyl alcohol......	0·0359	24·0	—	2·06	571·1	1970
,, ...	,,	24·5	22	2·05	568·4	1961

Camphanoquinoxaline, $C_8H_{14} < {C:N \atop C:N} > C_6H_4$
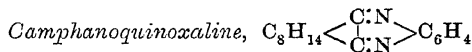
The quinoxaline derivative is obtained quantitatively by heating on the water-bath alcoholic solutions of camphorquinone and o-phenylenediamine. On dilution with water, it separates as an oil, which on rubbing becomes pasty and then solidifies. It is purified by dissolving in alcohol and precipitating with water, being obtained as a white, amorphous substance melting at 77—78°. It is very readily soluble in methyl or ethyl alcohol, acetone, glacial acetic acid, ether, benzene, light petroleum, carbon disulphide, or chloroform, and insoluble in water :

0·1725 gave 18·55 c.c. N_2 at 30·5° and 759·5 mm.   N = 12·1.
    $C_{16}H_{18}N_2$ requires N = 11·76 per cent.

The rotatory power determinations gave the following values :

Solvent.	Substance. Gram.	Temperature.	Time in hours.		$[\alpha]_D$.	$[M]_D$.
Ethyl alcohol .	0·2980	23·5°		$+0·97°$	$+32·4°$	$+77·1°$
		24·0	$8\frac{1}{2}$	0·94	31·4	74·71
,, ...		23·0	$23\frac{1}{2}$	0·94	31·4	74·71
Chloroform	0·3979	28·0	—	1·14	28·51	67·86
	,,	27·0	18	1·17	29·26	69·65
Methyl alcohol......	0·4254	30·0		1·43	33·45	79·6

m-*Phenylenebisiminocamphor*, $C_8H_{14} {<}^{C:N \cdot C_6H_4 \cdot N:C}_{CO \qquad\quad OC} {>} C_8H_{14}$.
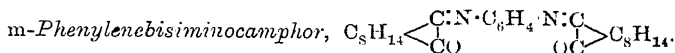
An alcoholic solution of camphorquinone (2 mols.) was added to an aqueous solution of *m*-phenylenediamine hydrochloride mixed with excess of sodium acetate, and heated for half an hour on the water-bath. The condensation product was obtained as an oil, which solidified on keeping and crystallised from dilute alcohol in yellow needles melting at 150—151°.

It is very readily soluble in methyl or ethyl alcohol, acetic acid, chloroform, ether, or pyridine, and insoluble in water:

0·1300 gave 8·25 c.c. N_2 at 31° and 760 mm. $N = 7·16$.

$C_{26}H_{32}O_2N_2$ requires $N = 6·93$ per cent.

The same substance was also obtained when camphorquinone and *m*-phenylenediamine were condensed in molecular proportions.

The rotatory power determinations gave the following values:

Solvent.	Substance. Gram.	Temperature.	Time in hours.	α_D.	$[\alpha]_D$.	$[M]_D$.
Methyl alcohol......	0·0193	30·5°	—	$+1·23'$	$+634·1°$	$+2563°$
Chloroform	0·0395	29·0	—	0·52	658·3	2660
	(in 100 c.c.)					
,, ...	,,	28·0	21	0·53	671·0	2710

More concentrated solutions were too dark for observations to be made on them.

o-*Methoxyphenyliminocamphor*, $C_8H_{14} {<}^{C:N \cdot C_6H_4 \cdot O \cdot CH_3}_{CO}$
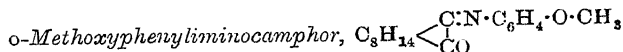
Camphorquinone and *o*-anisidine were mixed in molecular proportions, a little anhydrous sodium sulphate was added, and the whole heated on the water-bath for four hours. On cooling the product, it was dissolved in alcohol and precipitated by water. It crystallised from dilute alcohol in pale yellow prisms melting at 125—126°.

The substance is very readily soluble in methyl or ethyl alcohol, chloroform, ether, or acetic acid, and insoluble in water:

0·1135 gave 5·6 c.c. N_2 at 28° and 759 mm. $N = 5·61$.

$C_{17}H_{21}O_2N$ requires $N = 5·2$ per cent.

z* 2

The rotatory power determinations gave the following values. The solution was somewhat dark, and therefore difficult to read:

	Substance. Gram.	Temperature.	Time in hours.	a_D.	$[a]_D$.	$[M]_D$.
Solvent. Chloroform	0·0639	27°	—	+1·45°	+225·8°	+612·0°
	..	28	27	1·47	228·9	620·3

Condensations between camphorquinone and *m*-nitro-*p*-toluidine, *o*-, *m*-, and *p*-aminobenzoic acids, could not be effected.

This work was carried out at Dacca College. It is now being continued at Government College, Lahore.

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XLVI.—*The Nitration of Diphenylethylenediamine.*

By GEORGE MACDONALD BENNETT.

IT was shown by Mills in 1900 (T., **77**, 1020) that diphenylethylenediamine, $C_6H_5 \cdot NH \cdot CH_2 \cdot CH_2 \cdot NH \cdot C_6H_5$, may be nitrated in glacial acetic acid solution with the production of two isomeric tetranitro-derivatives, one melting at 303°, the other at 85°, the latter being much the more readily soluble in various solvents, and easily converted into the former by boiling its solution in acetone.

The close relationship between diphenylethylenediamine and monomethylaniline made it probable that an octanitro-derivative of the former might be obtained, analogous to trinitrophenylmethylnitroamine, $C_6H_2(NO_2)_3 \cdot NMe \cdot NO_2$. This proved to be the case, and the expected hexanitrodiphenylethylenedinitroamine, $[C_6H_2(NO_2)_3 \cdot N(NO_2) \cdot CH_2 \cdot]_2$, was isolated, either by nitrating the base in sulphuric acid, using a large excess of fuming nitric acid, or by using little more than the theoretical amount of nitric acid in the presence of fuming sulphuric acid.

From the products of the reaction there was also isolated a small quantity of a hexanitro-derivative, which must be isomeric with the compound melting at 230° obtained by Jedlicka (*J. pr. Chem.*, 1893, [ii], **48**, 204) by the interaction of ethylenediamine and either trinitroanisole or picryl chloride. This new hexanitrodiphenylethylenediamine and the Mills's tetranitro-compound (m. p. 85°), which it resembles closely in properties, are probably tetra- and di-nitrodiphenylethylenedinitroamines.

<div style="text-align:center">

EXPERIMENTAL.

Preparation of Diphenylethylenediamine.

</div>

The base has hitherto been prepared by the interaction of aniline and ethylene dibromide (Morley, *Ber.*, 1879, **12**, 1794), but it may be equally readily obtained by using the dichloride, the mixture of the latter with four molecular proportions of aniline being boiled for three-quarters of an hour. The reaction is much less violent than with the bromide. The base may be conveniently purified in the form of its *sulphate*, $C_{14}H_{16}N_2,H_2SO_4,H_2O$, which crystallises from hot water in colourless needles, being sparingly soluble in the cold:

1·502 (air-dried) lost in a vacuum 0·079. $H_2O = 5·3$.

$C_{14}H_{16}N_2,H_2SO_4,H_2O$ requires $H_2O = 5·8$ per cent.

0·3914 required 23·98 c.c. $N/10$-NaOH. Calc., 23·86 c.c.

<div style="text-align:center">

2 : 4 : 6 : 2′ : 4′ : 6′-*Hexanitrodiphenylethylenedinitroamine.*

</div>

Fifteen grams of the sulphate (dried at 110°) were dissolved in 100 grams of sulphuric acid (97 per cent.), and the solution was run slowly into 60 c.c. of fuming nitric acid (D 1·52) kept vigorously stirred at 30—35°. The temperature of the mixture was then slowly raised, and kept finally at 80° during an hour. When the product was cold, the solid which had been precipitated was collected on asbestos and washed successively with dilute sulphuric acid (70 per cent.), water, sodium carbonate solution, and finally with water. There remained, after drying, 19 grams of a yellow, sandy powder which melted and decomposed at 200°. A similar result was obtained when the nitration was carried out in the presence of fuming sulphuric acid, using the calculated amount (eight molecular proportions) of nitric acid. By washing the sandy product with ethyl acetate or, better, by recrystallisation from acetone, in which it is sparingly soluble, the octanitro-derivative was obtained as a pale yellow, crystalline powder melting and decomposing at 213° (uncorr.):

0·2771 gave 0·2974 CO_2 and 0·0400 H_2O. $C = 29·3$; $H = 1·61$.

0·1315 ,, 26·75 c.c. N_2 (moist) at 15° and 763 mm. $N = 24·03$.

$C_{14}H_8O_{16}N_{10}$ requires $C = 29·3$; $H = 1·4$; $N = 24·5$ per cent.

This compound is insoluble in the ordinary organic solvents, with the exception of ethyl acetate and acetone, in which it is appreciably soluble. It may be obtained in minute, lemon-yellow crystals

by crystallisation from nitrobenzene, in which it is readily soluble. It explodes on sudden heating. When heated with a concentrated solution of sodium hydroxide, it is decomposed, with the formation of picric acid.

Hexanitro-derivative.

The dark-coloured mother liquors from the purification of the crude octanitro-derivative by means of ethyl acetate or acetone left, on evaporation, a dark brown powder which appeared to be a mixture, and from which crystalline products could not readily be isolated. By fractional precipitation of its solution in glacial acetic acid by the addition of water, an amorphous, canary-yellow powder was obtained which melted and decomposed at 70°, and appeared to be a hexanitro-derivative:

0·1834 gave 0·2362 CO_2 and 0·0413 H_2O.   C = 34·6; H = 2·5.

$C_{14}H_{10}O_{12}N_8$ requires C = 34·8; H = 2·07 per cent.

It is readily soluble in acetone, glacial acetic acid, ethyl acetate, or nitrobenzene, but practically insoluble in chloroform, benzene, carbon tetrachloride, or light petroleum.

XLVII.—The Propagation of Flame in Mixtures of Acetylene and Air.

By WALTER MASON and RICHARD VERNON WHEELER.

MEASUREMENTS of the speed of the "uniform movement" during the horizontal propagation of flame in mixtures of acetylene and air have recently been made by Haward and Sastry (T., 1917, **111**, 841) in revision of earlier determinations by Le Chatelier (*Compt. rend.*, 1895, **121**, 1144).

The electrical method of measuring the speeds of the flames employed by Haward and Sastry was found by them to be unsatisfactory when the propagation took place in a tube of as large a diameter as 25 mm., the duration of the uniform movement being too short and its speed too great to allow of sufficiently

accurate records being obtained. For this reason, they reported only results procured by using a tube 12 mm. in diameter. The tube employed by Le Chatelier was 40 mm. in diameter.

The maximum speeds during the uniform movement were found to be with mixtures containing from 8 to 10 per cent. of acetylene, and were: in a 12-mm. tube (Haward and Sastry), 260 cm. per second; in a 40-mm. tube (Le Chatelier), about 600 cm. per second.

From the results obtained with inflammable gases other than acetylene (see, for example, T., 1917, **111**, 1044), one would not expect to find the speed of the uniform movement of flame so dependent on the diameter as these figures indicate. Means were therefore sought to compare the speeds in tubes of different diameters. From the appearance of the flames, it seemed probable that they would have sufficient actinic power to affect a sensitive photographic film during quite a short time of exposure, so that it should be possible to employ the photographic method of recording the speeds of flames devised by Mallard and Le Chatelier (*Ann. des Mines*, 1883, [viii], **4**, 312) for use with mixtures of carbon disulphide with oxygen or nitric oxide, the flames of which are highly actinic. On trial, it was found that over the whole range of inflammable mixtures of acetylene and air a sufficiently definite image of the flame was obtained on a highly sensitive photographic film moving at a rapid speed in a direction normal to the direction of propagation of flame.

This method, described in detail in the experimental portion of this paper, was therefore adopted for the determinations of the speeds of the uniform movement of flame in mixtures of acetylene and air herein recorded, tubes 12·5, 25, 50, and 90 mm. in diameter being used.

Apart from its value in enabling the mean speed of propagation of flame over a measured distance to be calculated, the photographic method enables a detailed study to be made of the manner of movement of the flame. Such a study has been made, with particular reference to the phenomena resulting in and accompanying the detonation wave, by Dixon (*Phil. Trans.*, 1903, [*A*], **200**, 315), who has brought flame "analysis" by these means to the acme of perfection.

Mallard and Le Chatelier's observations on the mode of propagation of flame, as revealed by photographs, have frequently been epitomised; but it is desirable to recall them again, preferably in Le Chatelier's words, which are as follow ("Le Carbone," p. 273, Paris, 1908):

"On constate dans ces conditions, lorsque l'inflammation a été mise du côté de l'extrémité ouverte du tube, que la flamme se

propage d'abord avec une vitesse sensiblement uniforme; la courbe enregistrée est alors une droite, plus ou moins inclinée; il se développe bientôt des mouvements vibratoires dans la masse gazeuse qui prennent parfois une violence extraordinaire, la courbe présente des ondulations très accentuées; enfin, dans certains cas, la propagation de l'inflammation devient brusquement, en quelque sorte, instantanée, du moins tellement rapide qu'il est bien difficile de reconnaître l'existence d'une vitesse définie."

This description is founded mainly on the results of experiments with mixtures of carbon disulphide and nitric oxide, for with no other inflammable gas was the flame sufficiently rich in actinic rays to affect satisfactorily the rapidly moving sensitised paper (gelatino-bromide paper) which Mallard and Le Chatelier used. The description is, however, intended to apply to the propagation of flame in most gaseous mixtures ignited under the conditions specified.

It will be understood that an advantage of this method of determining the speed of uniform movement of flame, over such as involve the fusion of screen-wires at fixed positions along its path, lies in the assurance given by the photograph that no part of the " vibratory movement," during which the flame may momentarily attain a very rapid speed, is included in the measurement.

In the present instance, the necessity of avoiding the development of the detonation wave, with consequent shattering of the glass apparatus, demanded that tubes of not much greater length than 150 cm. should be employed. With such short tubes, the uniform movement may give place to the vibratory movement at a distance of less than 20 cm. from the point of ignition (the open end of the tube). It is difficult to record accurately the times of fusion, by rapidly moving flames, of screen-wires placed so close together as this.

There is little doubt but that the inadvertent inclusion of part of the vibratory movement of the flame in the measurement of the speed of the uniform movement has been responsible for some of the discrepant results reported by different experimenters. It would seem most probable that herein lies the explanation of the high velocities recorded by Le Chatelier for the uniform movement of flame in mixtures of acetylene and air in a tube of 40 mm. diameter; for whilst the photographic method of recording the speeds confirms the results obtained by Haward and Sastry when using a tube 12 mm. in diameter, neither in a 50 mm. nor even in a 90 mm. tube did the flames attain during the uniform movement such high speeds as in Le Chatelier's experiments. The maximum speed of flame shown by the photographs during the uniform

movement was 335 cm. per second, for mixtures containing between 9 and 10 per cent. of acetylene (tube 90 mm. in diameter); as compared with 600 cm. per second recorded by Le Chatelier for like mixtures (tube 40 mm. in diameter).

In Fig. 1 the results obtained in the four tubes of different diameters are plotted as speed–percentage curves. The influence of the diameter of the tube on the speed of the uniform movement of flame in mixtures of acetylene and air is shown by this diagram to be of the same degree as with other inflammable gases. For example, the maximum speeds may be compared with those for

FIG. 1.
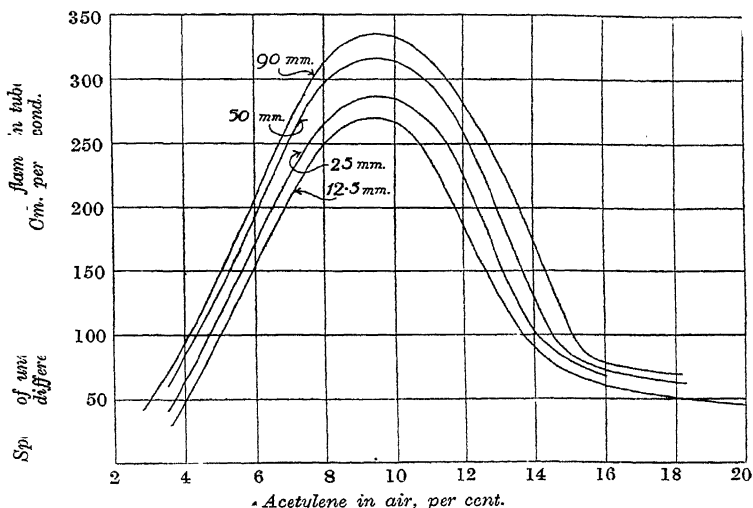
mixtures of methane and air in tubes of the same diameters (T., 1917, **111**, 1052), as follows :

Speed of uniform movement of flame.
Cm. per sec.

Diameter of tube in mm.	Methane–Air (9·5 per cent. CH$_4$)	Acetylene–Air (9·5 per cent C$_2$H$_2$)	Ratio.
25	67	285	4·2
50	93	315	3·4
90	105	335	3·2

The mixture at the lower limit of inflammability, horizontal propagation of flame, contains 2·7 per cent. of acetylene. The upper limit is indeterminate, exothermic decomposition of excess.

of acetylene, with deposition of carbon, taking place after a percentage of acetylene of about 17 is exceeded.   The speed at which
flame travels in the latter mixtures is slow, but does not decrease
much with increased acetylene content, as is shown in Fig. 1.
According to Le Chatelier, propagation of flame can be obtained
(in a tube 40 mm. in diameter) with mixtures containing up to
64 per cent. of acetylene, the speed at the limit being about 5 cm.
per second.

Figs. 2—6 reproduce some characteristic appearances of the
flames.   Each tube was partly covered with black paper, leaving a
horizontal slit 5 mm. broad and 30 cm. long, which was focussed
on the revolving film.   A strip of paper 1 cm. broad divided the
slit into two portions, each 14·5 cm. long; this strip appears as a
black central line on the photographs.   The slit began 10 cm.
from the open end, where ignition was effected.

In each instance the flame should be pictured as travelling
horizontally from left to right over a measured distance, while the
film is moving vertically at a known speed.   A curve is thus
traced, each point on which has for abscissa the distance travelled
by the flame and for ordinate the time that has elapsed since its
first appearance at the slit.

Fig. 2. C_2H_2, 5·40 *per cent.*—A mixture of the same composition inflamed in tubes of 12·5, 25, and 50 mm. internal
diameter and photographed on the same film, the peripheral speed
of the drum to which it was attached being 57·6 cm. per second
in each instance.   The increase of speed of flame with increased
diameter of tube is well illustrated by this photograph, and is at
once apparent from the angles of inclination of the images.   The
speeds are: 12·5 mm. tube (*A*), 120 cm. per sec.; 25 mm. tube
(*B*), 140 cm. per sec.; 50 mm. tube (*C*), 160 cm. per sec.

Fig. 3. C_2H_2, 15·00 *per cent.*—A mixture of the same composition inflamed in tubes of 12·5, 25, and 50 mm. internal
diameter.   The speed of the film in each instance was 96 cm. per
second.   It will be seen that with each of the tubes of larger
diameter the uniform movement gave place to the vibratory movement after the flame had traversed half the length of the slit, a
distance of about 25 cm. from the open end of the tube.   The
increase in the mean speed of the flame when this transition takes
place is well marked.*   Only the left-hand halves of the curves

---

* It is necessary here to note that a distinction must be drawn between
the vibrations of large amplitude, accompanied by enhanced mean speed of
flame, and the undulations, which are without effect on the speed of the
flame, apparent during the " uniform movement " in the larger tubes.   The
cause of these undulations is explained later.

FIG. 2
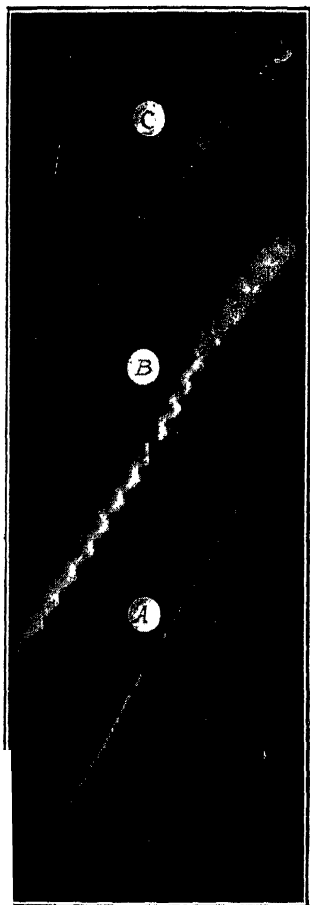
FIG. 3.
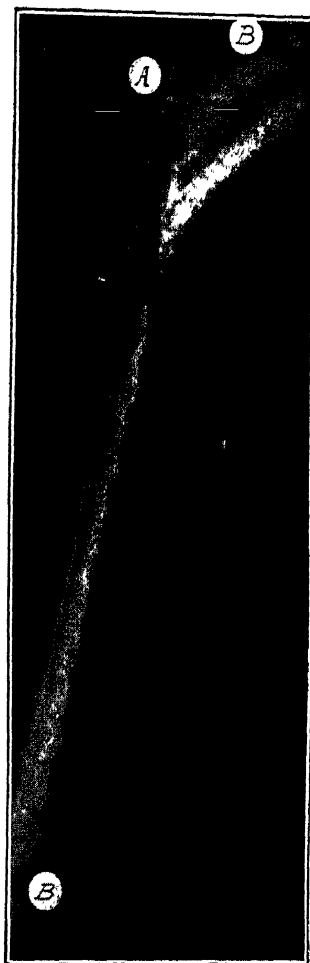
FIG.
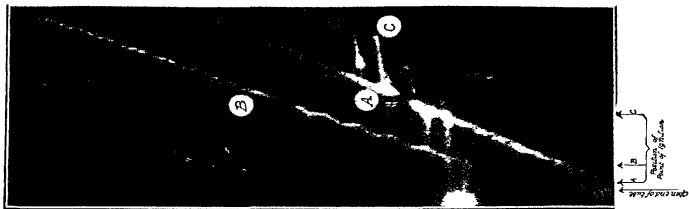
FIG.
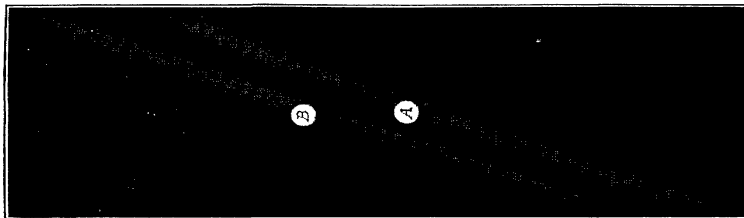
FIG.

Fig.

FIG.
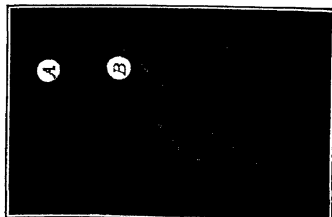
can be used for calculating the speeds of the uniform movement, which are: 12·5 mm. tube (A), 70 cm. per sec.; 25 mm. tube (B), 78 cm. per sec.; 50 mm. tube (unlettered), 85 cm. per sec.

Fig. 4.—Flame travelling in a tube 90 mm. in diameter, the mixture containing 9·45 per cent. of acetylene. Speed of film, 96 cm. per sec. The speed of the uniform movement of this flame (335 cm. per sec.) is the fastest recorded for any mixture of acetylene and air during the course of this research.

Fig. 5.—Flame travelling in a mixture containing 15·55 per cent. of acetylene photographed in a tube of 25 mm. internal diameter. Speed of film, 96 cm. per sec. This mixture contains a considerable excess of acetylene above that required for complete combustion of the oxygen. Secondary combustion took place, air being drawn in from the open end of the tube, whilst the initial flame was travelling a distance of 27—28 cm.; the vibratory movement, with enhanced mean speed of the flame, was then developed.

A feature, common to all the photographs of the flames in the tubes of larger diameter, is the undulating character of the flame front during the uniform movement. The undulations are due to resonance induced in the tubes at the moment of ignition, in part by the compression wave or pulse produced when the suddenly ignited gases expand, and in part by the pulse or train of pulses arising from the source of ignition itself. This, in the majority of the experiments, was a series of secondary discharges across a 3 mm. gap 3 cm. from the open end of each tube, obtained from a "6-inch" induction coil with a current of 10 amperes in the primary circuit. A single such discharge produces a pulse of considerable intensity (see, for example, Töpler, *Ann. Phys. Chem.*, 1867, [ii], **131**, 33; 1868, **134**, 194), and it is clear from Fig. 6 that the series of discharges used to cause ignition of the mixtures was largely operative in producing the more pronounced undulations of the flame during the uniform movement.

For this photograph (Fig. 6), a mixture containing 5·4 per cent. of acetylene was ignited in a tube 25 mm. in diameter (A) by means of a small hydrogen flame held at the mouth of the tube, and (B) by the secondary discharge at the spark-gap 3 cm. within. Both photographs were taken on the same film (speed 55 cm. per second), and the images were good enough to fall close together, so that comparison between them is facilitated. It will be seen that A exhibits but slight signs of an undulatory motion of the flame during the uniform movement, whilst in B the undulations are well defined and similar in general character to those appearing in the majority of the photographs. The mean speed of the

flame (141 cm. per second) is not affected by the undulations.

No rigid uniformity in the manner of ignition of the mixtures was attempted when determining the speeds recorded in Fig. 1; for, provided that the flame is allowed to travel a sufficient distance before measurement of the speed of the uniform movement is made, the initial impetus given to the flame by the spark dies away. A tapping key was employed, the trembler of the induction coil being allowed to function in the usual manner, and no doubt the discharge was maintained during a longer period in some instances than in others. Experiment showed that prolonged passage of the discharge after ignition had been effected sometimes resulted in the appearance in the photographs of the flames of small undulations superposed on the main undulations, but did not otherwise affect their character.

There remain to be considered the faint undulations apparent in Fig. 6, A. These are evidently due to resonance set up in the column of gases in the tubes by the slight shock imparted to it at the moment of ignition, for if great care be taken to avoid any disturbance at the mouth of the tube when igniting the gases, no undulations of the flame appear. In Fig. 7 are reproduced the photographs of flames travelling in a mixture containing 5·15 per cent. of acetylene. For (A) ignition was by a small jet of burning hydrogen introduced through a hole 4 cm. from the open end of the tube, whilst for (B) a large, flat flame of hydrogen, which more than covered the cross-section of the tube, was used, and this was held momentarily across the mouth of the tube in such a manner that ignition of the mixture took place there simultaneously over the whole surface. With the small source of ignition at a point 4 cm. within the tube, an undulatory motion is imparted to the flame of a more pronounced character than when a similar small source of ignition is held at the mouth of the tube (Fig. 6, A). With the large source of ignition (B), the propagation of flame is initially absolutely uniform. The speed of the film for these photographs was 96 cm. per second.

Fig. 8 shows the effect of varying the intensity of the compression wave or pulse produced on ignition by varying the volume of mixture contained between the point of ignition and the open end of the tube. The photographs record the progress of the flame from the point of ignition, which was 1 cm. within the tube for (A), 4·5 cm. within for (B), and 12 cm. within for (C). A mixture containing 5·8 per cent. of acetylene was used, and the tube was 25 mm. in diameter. The speed of the film was 100 cm. per

second. Ignition was by a single discharge across a 3 mm. gap produced by breaking a current of 6·6 amperes in the primary of a "10-inch" X-ray coil, the trembler of which was locked.

The "uniform movement" of the flame lies towards the right-hand side of each photograph, that direction of travel being towards the closed end of the tube. Towards the open end the flames travel rapidly, and some of the mixture is projected into the air and burns there. It is clear that the larger the volume of the mixture thus rapidly ignited, and the more intense in consequence the compression wave produced, the greater is the amplitude of the undulations produced in the uniform movement of the flame. When the point of ignition is 12 cm. within the tube, the motion of the flame cannot be regarded as "uniform" at all. (In this connexion, see T., 1917, **111**, 1055.)

It may be remarked that the undulatory motion of the flames, even when accentuated by the use of a powerful secondary discharge to ignite the mixtures, is not apparent from direct observation. Its occurrence is rendered evident, however, not only by photographic means, but sometimes also by the appearance along the glass tubes of rings of moisture deposited at regular intervals after the flames have passed. Neyreneuf (*Compt. rend.*, 1880, **91**, 321) appears to have obtained similar effects in short tubes coated on the inside with paraffin wax.

The proof that these undulations are indeed resonance effects lies in the close correspondence between their frequencies as determined from the photographs and as calculated from the dimensions of the tubes. Each tube being closed at one end and open at the other, the mode of vibration of the column of gases to give the fundamental tone results, according to Bernoulli's theorem, in an approximate frequency $n = u/4l$, u being the velocity of sound in the gases and l the length of the tube. This approximation assumes a loop, with no pressure variation, at the open end of the tube, a condition which does not obtain. An "end correction" must be applied, which with flanged pipes amounts to about 0·82 r, and with unflanged pipes to about 0·60 r (see Rayleigh, "The Theory of Sound," Vol. 2, p. 183. London, 1896). That is to say, the length of the tube must be increased by 0·82 r if flanged and by 0·60 r if unflanged before Bernouilli's theorem is applied.

Of the tubes used in the experiments, that of 50 mm. diameter alone was flanged. The observed frequencies of the undulations during the uniform movement of the flames, the dimensions of the tubes, and the calculated frequencies for the fundamental tone

during the longitudinal vibration of air in cylindrical pipes of those dimensions, are given in the table that follows:

Frequency of undulations during uniform movement of flame.	Dimensions of tube		Calculated frequency of fundamental tone of tube.
	Length.	Diameter.	
63	130 cm.	1·25 cm.	63·5
59	141	2·5	58·4
65	126	5·0 (flanged)	64·8
58	140	9·0	58·1

The value taken for the velocity of sound when calculating the frequencies of the fundamental tones of the tubes was 332 m. per second, the velocity in open air at 15°. The velocity in the mixtures in the tubes would vary slightly with the composition of the mixture and the diameter of the tube, but not to a sufficient extent to affect seriously the calculated frequency.

Experimental.

The only part of the experimental arrangements requiring further description is the camera. This consisted of a light-tight box furnished with a lens of quartz 13 cm. in diameter, and containing a drum for the reception of the film, which could be revolved at a high speed.

The focal length of the lens was 17 cm., and its position was fixed once and for all in relation to (1) the tube to be photographed, and (2) the film, so that the size of the image obtained was nearly one-quarter that of the object, the distance of the film from the lens being 20·5 cm.

The drum was 47 cm. in circumference and 10 cm. wide. Its spindle projected at either end through the sides of the camera, and carried at the one end a pulley to receive the drive of an electric motor and at the other end a reduction gearing. This gearing communicated with another drum, of the same diameter as that within the camera, used to receive, on a smoked paper chart, the record of a tuning-fork. The speeds of revolution of the two drums were as 1:32.

All the records of speeds obtained by the photographic method are given in the table that follows. As a check on the method, a series of determinations was made in the 12 mm. tube, using the "screen-wire" method as employed by Haward and Sastry; these determinations are placed within brackets in the table.

Speed of uniform movement of flame.

Diameter of tube in mm. =	12·5	25	50	90
Acetylene in air. Per cent.				
2·75	—	—	—	40
3·30	(26)	—	—	—
3·45	25	41	60	—
3·55	—	—	—	69
4·00	(55)	—	—	—
4·40	—	—	—	115
4·60	82	95	115	—
5·30	(120)	—	—	—
5·40	120	140	160	—
5·80	—	—	—	195
6·00	(155)	—	—	—
6·10	158	172	205	—
7·00	—	—	—	265
7·05	205	225	250	—
7·15	(205)	—	—	—
7·40	220	240	270	—
7·95	—	—	—	310
8·00	(252)	—	—	—
8·15	258	270	303	—
8·60	(260)	—	—	—
8·90	265	282	312	—
9·00	(268)	—	—	—
9·45	(265)	—	—	335
9·90	266	280	310	—
10·35	260 (265)	278	304	—
10·55	—	—	—	320
10·65	(255)	—	—	—
11·00	(235)	—	—	—
11·60	206 (210)	245	283	—
11·85	—	—	—	285
12·30	—	—	—	260
12·40	(160)	—	—	—
12·50	150	191	230	—
13·25	115	145	175	220
13·30	(115)	—	—	—
14·00	90	100	115	—
15·10	70	78	85	—
15·30	—	—	—	84
15·60	(65)	—	—	—
16·00	60	68	72	—
18·20	—	—	60	70

The acetylene was obtained compressed in cylinders, without acetone as solvent, and was of a high degree of purity. The air mixtures were made in metal gas-holders over brine, and were analysed before use.

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XLVIII.—*The Preparation of Diacetonamine.*

By Arthur Ernest Everest.

The methods for the preparation of diacetonamine which are described in the literature are laborious and by no means satisfactory, and this applies whether the preparation is through mesityl oxide or by the direct action of ammonia on acetone.

Having need of considerable quantities of the compound, as the starting point for synthetic work, the author tried to find a method which would be both simple in action and satisfactory in respect of yield. The process described below, which was the result of the work, is successful in both respects, and furthermore eliminates almost completely the laborious recovery of mixtures of alcohol and acetone which are formed in the usual process of preparation from acetone and ammonia (see the table below). It enables considerable quantities of diacetonamine to be prepared with ease and comparative rapidity, and thereby makes this product much more available as a starting point for synthetic work.

One of the chief difficulties in the production of diacetonamine from acetone and ammonia is the comparatively small amount of ammonia which acetone will dissolve, a fact that necessitates several slow re-saturations being resorted to at intervals of five to seven days. Even when this course is adopted, a large proportion of the acetone remains unchanged. The author has made use of anhydrous calcium chloride to obviate this difficulty. By this means, the whole of the ammonia required can be passed into the reaction mixture in quite a short time, and, moreover, not only does the calcium chloride store up the requisite ammonia, but the water formed as the reaction proceeds is taken up by it, whereby a concentrated solution is formed which separates as a distinct layer and can be removed when the reaction is completed.

Experimental.

Acetone (1160 grams) and anhydrous calcium chloride (200 grams) were introduced into a vessel fitted with a reflux condenser (to prevent loss of acetone during the introduction of ammonia) and an inlet for ammonia. The vessel was then placed in cold water and ammonia (from a cylinder) blown into the mixture as rapidly as the liquid would absorb it (100 grams of ammonia were introduced in quite a short time without any appreciable loss).

Much heat was developed during the addition of the ammonia, but with an effective condenser no loss resulted from this.   The introduction of ammonia was continued until the amount absorbed was equal to the weight of the calcium chloride used (200 grams).   If it was found that the liquid became nearly saturated before the requisite amount of ammonia had been added (this was rarely the case), the addition of ammonia was stopped, the vessel allowed to remain some eight to ten hours (say overnight), and a further amount of ammonia then added.   Before the whole of the ammonia had been introduced, water had usually commenced to separate, a fact that had no detrimental effect on the result.

When 200 grams of ammonia had been blown in, the vessel was allowed to remain at the ordinary temperature for eight to nine days.   It was found to be advantageous to shake well once a day during this period.   As the reaction proceeded, the compound of calcium chloride and ammonia decomposed, and the products dissolved in the water formed by the reaction, the calcium chloride solution thus produced forming the lower layer in the vessel. Towards the end of the reaction, the upper layer became quite viscous and developed a pale yellow colour, whilst the odour of the amine became noticeable alongside that of ammonia.

When the reaction was completed, the layers were separated, care being taken that all the calcium chloride was removed, as when this was not done, considerable trouble was caused in the filtrations later by the calcium oxalate formed in working up the product.   The aqueous layer when extracted with ether yielded a small additional quantity of amine, but in general it was not considered profitable to carry out this operation, and the yields stated below do not include such extractions.

After separation, the amine layer (top) was placed in a vessel and dry air drawn rapidly through it for several hours, whereby a large proportion of the excess of ammonia was removed.   The liquid thus obtained possessed a strong odour of the amine.   The amount of oxalic acid required for the formation of the hydrogen oxalate was determined (by titration with standard oxalic acid), this was dissolved in alcohol, three times the volume of the reaction mixture being used, and the amine then poured slowly into the alcoholic solution, the whole being kept well agitated. Rectified spirit (B.P.) gave with this process as good results as absolute alcohol had given with other processes, this being due to the fact that the water produced in the reaction was removed, whilst in the older methods it remained in the reaction mixture.

When all the amine had been added, the product, without filtration, was placed in a distilling flask and distilled up to 75°, during

which process a small amount of a mixture of acetone and alcohol passed over (from 1160 grams of acetone, only about 45 grams remained unacted on and passed over in this mixture). At 75°, the distillation was discontinued, and the contents of the distilling flask were rapidly filtered hot. The filtrate, on cooling, deposited diacetonamine hydrogen oxalate in crystalline condition, which was collected, washed with alcohol, and dried. The solid residue from the hot filtration yielded a small additional quantity of the product when extracted with fresh hot alcohol. From the total mother liquors, a considerable further quantity of pure product was obtained by distilling them on a water-bath until nothing further passed over, allowing the residue to remain for about twenty-four hours in the cold, collecting the crystals which separated, and washing them with alcohol. A certain amount of syrup remained as a by-product, and in this a small amount of triacetonamine was detected.

By the above method, 800 grams of diacetonamine hydrogen oxalate (m. p. 125—127°), containing about 1 per cent. of ammonium hydrogen oxalate (see note at end of paper), could be regularly obtained. Of this yield, about 600 grams were obtained from the first deposition and about 200 grams from the liquors and by extraction of the solid residues.

The following table gives comparative results as obtained with the method described above (a), and by the direct action of ammonia on acetone without the use of calcium chloride (b).

	(a.)	(b.)
Acetone taken	1045 grams	2100 grams
,, recovered	45 ,,	1100 ,,
,, used	1000 ,,	1000 ,,
Acetone–alcohol mixture fractionated to recover acetone and alcohol ...	100 c.c.	2250 c.c.
Alcohol used	3 litres (rectified spirit, B.P.)	2½ litres (absolute).
,, recovered	All ; somewhat diluted.	All ; considerably di-luted.
Oxalic acid used	1050 grams.	1060 grams.
Time of keeping	8½—10 days.	24—28 days.
Number of saturations with ammonia	One.	4, at intervals of 5—7 days.
Ammonia used (anhydrous)	190 grams.	210 grams.
Yield	724 ,,	434 ,,
By-product : ammonium hydrogen oxalate	340 ,,	440 ,,

The work described above was carried out in the chemical laboratories of University College, Reading, in February, 1916, and the author desires to thank the Sectional Chemical Committee

of the Royal Society, at whose request the preparation of the diacetonamine was undertaken, for permission to publish the results.

<center>APPENDIX.</center>

Note on Diacetonamine Hydrogen Oxalate and Vinyldiacetonamine Oxalate.

<center>By ARTHUR ERNEST EVEREST and HAROLD ROGERSON.</center>

In connexion with the work on the new process for the preparation of diacetonamine described above, it was desirable that a ready means of checking the purity of samples of diacetonamine hydrogen oxalate and of vinyldiacetonamine oxalate should be available. It was further necessary to prove the identity of the products obtained.

In view of the fact that no melting points have been recorded in the literature for these substances, previous workers have at times resorted to the expedient of converting either of the above compounds into a salt of vinyldiacetonalkamine, liberating the free base, and determining the melting point of this. The fact that this method is obviously unsatisfactory, and that time did not permit of ultimate analysis, led one of us (A. E. E.) to test pure specimens of the above compounds for melting point. It was found that both could be identified by this means. At the same time, the other (H. R.), who was also preparing quantities of these compounds, had quite independently observed that they had sharp melting points. The determinations were therefore mutually confirmed by exchange of specimens.

<center>EXPERIMENTAL.</center>

<center>(a) *Diacetonamine Hydrogen Oxalate.*</center>

A pure specimen of diacetonamine hydrogen oxalate melts fairly sharply at 126—127° to a clear, colourless liquid which, on cooling, sets to a mass of crystals, which again melt at 126—127°. The presence of ammonium hydrogen oxalate in the product causes opalescence in the liquid that results on melting, but has little effect on the melting point. Thus:

Pure diacetonamine hydrogen oxalate melts to a clear liquid at 126—127°.

Pure diacetonamine hydrogen oxalate + 1 per cent. of ammonium hydrogen oxalate melts at 125·5—127°.

Pure diacetonamine hydrogen oxalate + 5 per cent. of ammonium hydrogen oxalate softens then melts at 124·5—126°.

Pure   diacetonamine   hydrogen   oxalate + 10   per   cent.   of ammonium hydrogen oxalate softens more noticeably then melts at 124—125·5°.

If much ammonium hydrogen oxalate is present in the sample, no melting point is observed, only a softening taking place.   This may account for the fact that no melting point has been recorded previously.

A rough approximation of the amount of ammonium hydrogen oxalate in a sample of diacetonamine hydrogen oxalate may be obtained by observation of the degree of opalescence shown when it melts, but for more accurate determinations an extraction of the diacetonamine salt from the sample by boiling absolute alcohol and weighing of the residue is recommended.

(b) *Vinyldiacetonamine Oxalate.*

When this compound is prepared from diacetonamine hydrogen oxalate which contains ammonium hydrogen oxalate, the latter passes through into the product.   The presence of ammonium hydrogen oxalate has the same effect on the melting point of vinyl-diacetonamine oxalate as it has on that of the diacetonamine salt. If sufficient of the ammonium salt is present, no melting point can be observed, mere shrinkage and change of colour taking place.

Pure   vinyldiacetonamine   oxalate,   prepared   from   pure   di-acetonamine hydrogen oxalate and freed from the latter and from oxalic acid by twice boiling with a fairly large quantity of absolute alcohol, filtering hot, and finally washing with boiling absolute alcohol and drying in a vacuum over concentrated sulphuric acid, melts sharply at 184—185° with the evolution of gas and develop-ment of a yellow colour.   The presence of diacetonamine hydrogen oxalate in the vinyl compound affects the melting point of the latter considerably and makes it less sharp.

These observations were made at University College, Reading, and at Guy's Hospital Medical School, in February, 1916.

XLIX.—*The Constitution of Maltose. A New Example of Degradation in the Sugar Group.*

By JAMES COLQUHOUN IRVINE and JAMES SCOTT DICK.

IN the following paper are described the principal results obtained in an investigation undertaken some years ago with the object of determining the constitution of maltose. The standard process was adopted of complete methylation of the disaccharide, followed by identification of the two alkylated sugars produced on hydrolysis, and the series of reactions as originally planned may be represented by the following synopsis:

Maltose   Methylmaltoside

                                        Tetramethyl glucose

        Heptamethyl methylmaltoside

                                        Trimethyl glucose
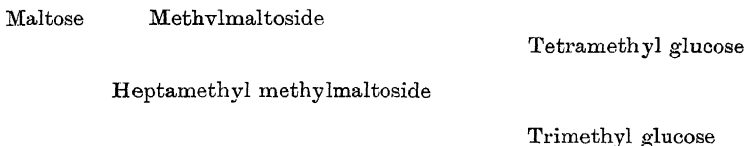
Although the above scheme has not been fully realised, it has been possible to confirm and supplement the earlier results of Purdie and Irvine (T., 1905, **87**, 1022), who showed that the non-reducing glucose component of maltose possesses the butylene–oxide structure, and thus yields crystalline tetramethyl glucose as one product of the above reactions.

This result establishes the constitution of one half of the disaccharide molecule, but, owing to an unexpected degradation of maltose encountered in the course of the work, we have been unable to isolate the trimethyl glucose which should be formed as a second hydrolysis product from a fully methylated maltoside. On the basis of the accepted constitution of maltose, the operation of the series of reactions should give, in addition to tetramethyl glucose, the butylene–oxide form of trimethyl glucose described by Purdie and Bridgett (T., 1903, **83**, 1037). This is shown below:

$$\overset{\llcorner\quad\quad\urcorner}{CH\cdot[CH\cdot OH]_2\cdot CH\cdot CH(OH)\cdot CH_2\cdot OH}$$

Non-reducing glucose component ;
should yield tetramethyl glucose.

O $<$

$$CH_2\cdot CH(OH)\cdot CH\cdot[CH\cdot OH]_2\cdot CH\cdot OH$$

Reducing glucose component ;
should yield trimethyl glucose.
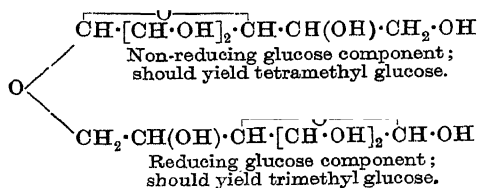
The identification of the particular form of trimethyl glucose to be expected is, however, difficult in view of the failure of this sugar to give crystalline derivatives, and accordingly, as a necessary preliminary to the present research, we re-examined the compound and determined its physical constants as standards of comparison. In addition, the constitution provisionally assigned to the sugar has been confirmed by a study of its decomposition products. When oxidised drastically by means of nitric acid, the essential product proved to be the monolactone of trimethylsaccharic acid,

$$CO_2H \cdot CH(OMe) \cdot \overset{\overbrace{\hspace{1.2cm}O\hspace{1.2cm}}}{CH \cdot [CH \cdot OMe]_2 \cdot CO} \; ,$$

a result which confirms the view that the primary alcohol group in the parent sugar is unsubstituted.

The data thus accumulated proved, however, of little service in the present research, which developed an unexpected but interesting complexity. In preparing the necessary methylmaltoside, we adopted the method described by Mills (*Chem. News*, 1912, **106**, 165), in which hepta-acetyliodomaltose is converted into the corresponding acetylated methylmaltoside and the acyl groups are removed by hydrolysis. In the light of subsequent events, this proved to be an unfortunate decision. The various reactions appeared to proceed normally, but, on applying the silver oxide process to the " β-methylmaltoside," we obtained, after three methylations followed by vacuum distillation, a colourless syrup which gave on analysis by Zeisel's method figures agreeing closely with those required for a *hexamethyl methylmaltoside*. In the belief that the methylation was incomplete, further treatments with the alkylating mixture were carried out, but this had no effect on the composition. As a second preparation gave precisely the same result, although the silver oxide reaction was repeated five times, and this was followed by two further methylations, one by means of methyl sulphate and the other by diazomethane, we were forced reluctantly to the conclusion that steric hindrance had interfered completely with the methylation of one hydroxyl group of the maltose molecule.

The results of combustions were indecisive, and the correct interpretation was forthcoming only when the supposed hexamethyl methylmaltoside was hydrolysed, and the two sugars thus produced were separated by distillation in the high vacuum of the Gaede pump. As already mentioned, crystalline tetramethyl glucose was readily obtained as the fraction of lower boiling point, but the remaining product distilled only with the greatest difficulty under

a pressure of 0·1 mm., and could not be induced to crystallise. Examination showed this viscous syrup to be a reducing sugar and to possess the composition of a *dimethyl pentose,* so that clear evidence was thus obtained that, at some stage of the successive reactions, degradation of the maltose molecule had taken place to give derivatives of a sugar containing eleven carbon atoms in the chain. Owing to the close coincidence in the calculated composi-tions of a highly methylated methylmaltoside and a hexamethyl methylglucopentoside, it was impossible to detect this degradation before hydrolysis, and, owing to the unexpected nature of the result, it was necessary to obtain confirmatory evidence. The dimethyl pentose was therefore converted successively into the corresponding dimethyl methylpentoside and trimethyl methyl-pentoside, and each compound gave on analysis figures which agree closely with the above explanation. Further, the values found for the specific rotations of these compounds agree with the idea that they are derivatives of arabinose, and the corresponding nomenclature is accordingly employed in the experimental part.

There is little doubt that the degradation took place during the decomposition of maltose octa-acetate by means of hydrogen iodide, and is due to a species of reduction which is unusual in the sugar group. No doubt such a reaction, when once commenced, would be progressive, but in the twelve experiments conducted by us, the change was approximately arrested at a stage when the main pro-duct consisted of a derivative of a C_{11} sugar. The maltose origin-ally used was of high purity, and the octa-acetate prepared from it also conformed to accepted standards. On the other hand, the supposed "hepta-acetyl methylmaltoside," obtained after reaction with hydrogen iodide followed by treatment with methyl alcohol, was abnormal. Although apparently a definite chemical in-dividual, we were unable by any process of crystallisation to raise the melting point above 115—117°, whereas the recorded values are higher (Fischer and Armstrong, 121—122°, 125—126°; Königs and Knorr, 128—129°). Fischer has, however, remarked on the difficulty in obtaining this compound pure, and as the method of preparation adopted by us might lead to the production of non-separable α- and β-forms showing a lower melting point, there was no reason at the time to doubt the nature of the compound.

The interruption of our collaboration, due to the War, has pre-vented us from studying the degradation of sugars by means of hydrogen iodide on more general lines, but the subject is evidently important, as the possibility is opened out of degrading maltose in an acid system and comparing the results with those already

obtained by regulated oxidation in alkaline solution (Lewis and Buckborough, *J. Amer. Chem. Soc.*, 1914, **36**, 2385).

Meanwhile, in a separate research, the results of which will be communicated at an early date, the complete structure of maltose has been established by a method free from the complications now described.

<div align="center">EXPERIMENTAL.</div>

<div align="center">*Preparation of Maltose Octa-acetate.*</div>

As the preparation of this compound in a pure condition presents considerable difficulty, an account may be given of the method which in our experience proved the most satisfactory.

Pure maltose was acetylated by means of acetic anhydride and sodium acetate in the manner described by Herzfeld (*Annalen*, 1883, **220**, 200), but the reaction was continued for thirty minutes, after which the hot syrup was poured into cold water. On stirring vigorously, the product solidified, and the disintegrated solid was collected, dissolved in alcohol, and the solution neutralised with barium carbonate. The filtered solution was then poured into water, and the solid acetate which separated was collected on a filter and thereafter dried in a vacuum. On extracting the dry crystals repeatedly with a large excess of boiling ether, the impurities remained undissolved, and on removal of the solvents from the united extracts, the acetate was obtained in good yield. One recrystallisation from hot alcohol was then sufficient to give the pure compound melting at 157°.

<div align="center">*Action of Hydrogen Iodide on Maltose Octa-acetate.*</div>

Sixty grams of the acetate, in portions of 5 grams, were treated in methylene chloride solution with carefully purified hydrogen iodide, as described by Mills (*loc. cit.*). The excess of the gas and the solvent were removed in a high vacuum, and the residual syrup was at once dissolved in dry methyl alcohol, and the solution shaken with silver carbonate until free from iodine. On concentration of the filtrate, the product crystallised readily, but even after repeated crystallisation the melting point could not be raised above 117°.

The yields obtained in the twelve preparations varied considerably, and were in no case more than 60 per cent. of the theoretical amount. Apparently an important factor is to minimise the time during which the acetate is in contact with hydrogen iodide to less than thirty minutes, and to remove the excess of the gas as rapidly

as possible. Otherwise the amount of syrup formed is increased and the proportion of crystalline product seriously diminished.

The removal of the acetyl groups from the supposed hepta-acetyl methylmaltoside was effected in the usual way by shaking with aqueous barium hydroxide, the ultimate product being a glucosidic syrup, which proved to be methylglucoarabinoside. Throughout all the above reactions, the customary precautions were taken to prevent molecular rupture, and the operations were thus extremely tedious.

Methylation of Methylglucoarabinoside.

No details of this reaction need be given, as it was conducted precisely as described in earlier papers dealing with the methylation of glucosides by means of silver oxide and methyl iodide. After two alkylations in methyl-alcoholic solution, the product was freely soluble in methyl iodide, and consequently no extraneous solvent was required in the final methylations. The product, which was a clear, viscid syrup, was purified by fractionation in a high vacuum, and the following table shows that successive treatments did not increase the methoxyl content above a fixed maximum.

Number of methylations.	B. p.	n_D.	Methoxyl.
4	188—190°/0·35 mm.	1·4692	50·34 per cent.
5	195°/0·1 mm.	1·4688	50·66 ,,
5	205—208°/0·4 mm.	1·4695	52·2, 50·79 per cent.
6	200—203°/0·4 mm.	1·4689	50·45 ,,

In a second preparation, otherwise duplicate, the treatment was extended by one methylation by means of methyl sulphate and sodium hydroxide, and finally by diazomethane in ethereal solution, but without alteration in the analytical figures or physical constants of the product. The mean of several consistent analyses gave:

$$C = 52·11; \quad H = 8·21; \quad OMe = 50·9 \text{ per cent.}$$

Heptamethyl methylmaltoside:

$C_{20}H_{38}O_{11}$ requires $C = 52·86$; $H = 8·37$; $OMe = 54·63$ per cent.

Hexamethyl methylmaltoside:

$C_{19}H_{36}O_{11}$ requires $C = 51·81$; $H = 8·18$; $OMe = 49·3$ per cent.

Hexamethyl methylglucoarabinoside:

$C_{18}H_{34}O_{10}$ requires $C = 52·68$; $H = 8·29$; $OMe = 52·9$ per cent.

The results fail to discriminate between the alternatives, and the molecular weight, determined in benzene solution by the cryoscopic method, was equally inconclusive.

Found: 425.

$C_{10}H_{36}O_{11}$ requires 440; $C_{18}H_{34}O_{10}$ requires 410.

On the evidence yielded by hydrolysis, the compound was finally shown to be essentially hexamethyl methylglucoarabinoside $(C_{18}H_{34}O_{10})$.

The new glucoside is a viscid, colourless syrup freely soluble in organic solvents generally, but less so in water. Presumably the specimen examined would consist of both α- and β-forms, so that the specific rotations have only a qualitative significance, but, as is usually the case with methylated compounds possessing the glucose configuration, the activity was but little affected by the nature of the solvent.

Solvent.	c.	$[\alpha]_D^{20°}$.
Water	4·875	+78·8°
Methyl alcohol	5·609	77·5
Ethyl alcohol..............	5·316	75·9
Acetone	5·103	76·9

Hydrolysis of Hexamethyl Methylglucoarabinoside.

Preliminary experiments showed that the double hydrolytic change of removing the glucosidic methyl group and liberating the two constituent aldoses was best effected by boiling a 5 per cent. solution of the above compound in 5 per cent. aqueous hydrochloric acid. This method was accordingly applied to 38 grams of the glucoside, boiling under reflux being continued until the rotation diminished to a constant value, which it did in thirty minutes. The acid was neutralised with barium carbonate, the filtered solution evaporated to dryness under diminished pressure, and the residue extracted with boiling alcohol. After removal of the alcohol, the residual syrup was dissolved in hot acetone, the solution being again filtered and evaporated. The mixed sugars produced in the hydrolysis were obtained in this way as a pale yellow syrup, and were separated by fractionation at the Gaede pump.

A definite first fraction, amounting to 40 per cent. of the total weight, was collected at 125°/0·5 mm. as a moderately mobile liquid, but the remainder of the material distilled only with the greatest difficulty, and presented the appearance of a glass. As much decomposition took place in the later stages of the distillation, no attempt was made, after the first preliminary trial, to distil this product, heating being continued only until the first fraction had been removed.

The more volatile sugar crystallised readily, and, after draining on porous porcelain and two recrystallisations from light petroleum,

was identified as butylene-oxidic tetramethyl glucose melting at 85—87°. (Found: C=50·62; H=8·41; OMe=52·46. $C_{10}H_{20}O_6$ requires C=50·85; H=8·47; OMe=52·54 per cent.)

Mutarotation in alcohol: Initial $[\alpha]_D^{20}$ +104·9° $\longrightarrow$ Final 83·9°.

Identification of Dimethyl Arabinose.—The less volatile sugar solidified on cooling to a glass, and no crystallising medium could be found for the compound, as it is very readily soluble in water or organic solvents, with the exception of light petroleum. It reduces Fehling's solution readily, and is thus a reducing sugar, but gave only syrupy products when treated with aniline, hydroxylamine, or with phenylhydrazine and acetic acid. In approximately 5 per cent. solution, the compound was dextrorotatory:

Solvent.	$[\alpha]_D^{20°}$.
Water	+57·7°
Ethyl alcohol	50·6
Acetone	56·9

Before determining the activity or the analytical composition, the compound was further purified from traces of tetramethyl glucose by solution in dry ether and the addition of light petroleum, after which the syrupy precipitate was dried in a high vacuum.

The mean of three consistent analyses showed that the sugar was neither the di- nor the tri-methyl glucose expected.

Found: C=47·63; H=7·99; OMe=35·28.

Dimethyl arabinose:

$C_7H_{14}O_5$ requires C=47·19; H=7·86; OMe=34·83 per cent.

Dimethyl glucose:

$C_8H_{16}O_6$ requires C=46·13; H=7·73; OMe=29·8 per cent.

Trimethyl glucose:

$C_9H_{18}O_6$ requires C=48·63; H=8·15; OMe=41·9 per cent.

All the results, and more particularly the methoxyl content, point to the idea that the sugar is a dimethyl arabinose, but further identification was obtained by converting the compound into the corresponding methylpentoside by Fischer's method.

Dimethyl methylarabinoside proved to be a colourless syrup (b. p. 120°/0·1 mm., n_D 1·4620) devoid of action on Fehling's solution until hydrolysed.

Found: C=50·38; H=8·60; OMe=48·9.

$C_8H_{16}O_5$ requires C=50·00; H=8·33; OMe=48·5 per cent.

Further confirmation of the composition of the parent sugar was obtained by subjecting the above pentoside to the silver oxide reaction, so as to produce trimethyl methylarabinoside, which was

isolated as a colourless, mobile liquid (b. p. 94—96°/0·08 mm., n_D 1·4460).

Found: C=52·18; H=8·80; OMe=60·1, 60·8.
$C_9H_{18}O_5$ requires C=52·42; H=8·73; OMe=60·2 per cent.

The whole series of analytical results thus consistently supports the view that all the compounds examined are derivatives of a pentose, and not of a hexose. Considering their method of formation, they would consist of mixtures of α- and β-forms, and consequently specific rotations need not be quoted, but the fact that in each case the compounds are strongly dextrorotatory justifies the opinion that they are derived from arabinose, and this is embodied in the nomenclature used.

Trimethyl α-Methylglucoside and Trimethyl Glucose.

The above compounds are already known, but were re-examined for reasons stated in the introduction. Both substances are viscid syrups and yield no crystalline derivatives, so that their identification rests chiefly on the determination of their specific rotations. Unfortunately, the values found by different observers show considerable variation, a fact which may be explained by the difficulty encountered in fractionating syrups of high boiling point under the vacua given by an ordinary water pump, and accordingly we conducted our final distillations under the highly diminished pressure of the Gaede pump.

Fifty grams of α-methylglucoside were dissolved in methyl alcohol and methylated by means of silver oxide (150 grams) and methyl iodide (183 grams), exactly as described by Purdie and Bridgett (*loc. cit.*). After two alkylations, the product was isolated in the usual way and subjected to systematic fractionation, as a result of which 29·5 grams of pure material were obtained after six distillations. The syrup boiled at 160—161°/10 mm., showed n_D 1·4606, and gave $[\alpha]_D^{20} + 134·6°$ in absolute alcohol, a value which is not far removed from the specific rotation quoted by Purdie and Irvine (T., 1903, **83**, 1021).

On hydrolysis with aqueous hydrochloric acid, the glucoside was converted into trimethyl glucose, the sugar being isolated in the customary manner, and purified by repeated distillations which were continued after satisfactory analytical figures were obtained. The final boiling point recorded was 152—155°/0·02 mm., but the refractive indices and specific rotations shown by the product of different preparations fluctuated widely, although the parent glucoside employed was apparently identical. The

extent of this variation is shown in the two extreme cases quoted below.

In the first preparation, the trimethyl methylglucoside used showed n_D 1·4606 and $[\alpha]_D^{20}$ +134·6° in methyl alcohol, whilst in the second the corresponding values were 1·4596 and 132·4. The trimethyl glucose obtained from these two sources showed :

	Preparation I.	Preparation II.
n_D	1·4780	1·4768
$[\alpha]_D^{20°}$ in water	+48·6°	+60·7°
$[\alpha]_D$ in methyl alcohol	48·3	65·3
$[\alpha]_D$ in acetone	46·2	58·8

In view of these results, there can be little doubt that the sugar and the glucoside from which it was prepared were mixtures of isomerides, and the identification of $\beta\gamma\xi$-trimethyl glucose must in the meantime depend on oxidation processes.

Oxidation of Trimethyl Glucose.

3·5 Grams of the sugar were dissolved in 50 c.c. of nitric acid (D 1·7), and the solution was heated to 80° in order to start the oxidation. Thereafter, the mixture was kept at 65° for three hours, then diluted with water, and evaporated to a syrup under diminished pressure. The process of dilution with water and subsequent evaporation was repeated four times, and was followed by three similar treatments, in which alcohol was used as the diluent. As the syrupy product darkened rapidly at 120°, no attempt was made to distil the compound, which was prepared for analysis by heating at 60°/0·3 mm. until constant in weight. Analysis showed the substance to be the monolactone of trimethylsaccharic acid.

Found : C=46·07 ; H=6·33 ; OMe=37·2.
$C_9H_{14}O_7$ requires C=46·13 ; H=6·02 ; OMe=39·7 per cent.

When dissolved in alcohol and rapidly titrated with $N/10$-sodium hydroxide, the first neutralisation corresponded with the presence of one carboxyl group, and thereafter the compound behaved as a typical lactone on further titration. The lactonic structure was confirmed by the fact that in absolute alcohol the specific rotation remained practically constant, but diminished to a permanent value when aqueous alcohol was used as solvent.

Solvent.	Initial $[\alpha]_D^{20°}$.		Final $[\alpha]_D$.
Absolute alcohol	+41·5°	$\rightarrow$	+43·0° in 48 hours.
50 per cent. alcohol .	43·2	$\rightarrow$	24·0 ,, ,,

L.—*Catalytic Racemisation of Ethyl* l-*Mandelate.*

By ALEX. MCKENZIE and HENRY WREN.

THE work described in the present communication was suggested by the following observations which have been recorded in the literature dealing with the phenomenon of racemisation.

(1) When an optically active ester is hydrolysed by alkali, it has frequently been found that the product is partly racemised; for example, the specific rotatory power of the barium salt obtained by the action of aqueous barium hydroxide on ethyl *l*-phenyl-ethoxyacetate was only about one-half that of the optically pure salt (McKenzie, T., 1899, **75**, 759). Occasionally, the racemisation is even complete; thus, when *l*-mandelic acid was alkylated by a mixture of *n*-propyl iodide and silver oxide, the phenylprop-oxyacetic acid isolated from the resulting ester was, contrary to expectation, optically inactive, a result which may now be attributed, in part at least, to the action of the alcoholic alkali employed for the hydrolysis of the ester.* Another example is afforded by the more recent observation of Rupe and Kerkovius (*Ber.*, 1912, **45**, 1398), who obtained optically inactive αβ-diphenyl-propionic acid as a consequence of the action of alcoholic alkali on *l*-menthyl *l*-αβ-diphenylpropionate. Moreover, McKenzie and Miss Widdows showed that the acid isolated from the product of the action of a very slight excess of dilute alcoholic potassium hydr-oxide on ethyl *d*-phenyl-*p*-tolylacetate was quite inactive.

(2) The gradual racemisation of *l*-mandelic acid when heated

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* References on the partial racemisation occurring during the action of alcoholic alkali on optically active esters are the following : McKenzie, T., 1904, **85**, 378, 1249 ; McKenzie and Thompson, T., 1905, **87**, 1004, T., 1907, **91**, 789 ; McKenzie and Müller, T., 1907, **91**, 1814 ; McKenzie and Humphries, T., 1909, **95**, 1105 ; McKenzie and Widdows, T., 1915, **107**, 702 ; Wren and Still, T., 1915, **107**, 1449 ; Wren and Williams, T., 1916, **109**, 573 ; Wren, T., 1918, **113**, 210.

with alkali was first observed by Holleman (*Rec. trav. chim.*, 1898, **17**, 323), whose observations were extended by McKenzie (T., 1904, **85**, 385) and by McKenzie and Thompson (T., 1905, **87**, 1020). The contrast between the action of aqueous- and ethyl-alcoholic alkali on an optically active acid was studied by McKenzie and Bate (T., 1915, **107**, 1681) in the case of *l*-phenylanilinoacetic acid; the effect of the ethyl-alcoholic sodium hydroxide as compared with that of the aqueous alkali was very pronounced, the recovered acids having the values $[\alpha]_D -4°$ and $-109°$ respectively, whilst the pure acid used had $[\alpha]_D -117·9°$ in acetone.

(3) The contrast between the behaviour of *l*-menthyl *l*-mandelate towards aqueous- and ethyl-alcoholic alkali, respectively, as examined by one of us (T., 1904, **85**, 1256) is highly significant. The mandelic acid recovered when the hydrolysis was carried out at 100° with the calculated quantity of aqueous alkali gave the value $[\alpha]_D -126·4°$ in aqueous solution, whereas with the calculated quantity of alcoholic potassium hydroxide at 25° the recovered acid had a much lower value, namely, $[\alpha]_D -36·3°$. It was clear from these results, and also from others (for example, in the case of phenyl-*p*-tolylacetic acid), that there is more liability for racemisation occurring during the hydrolysis of esters by alcoholic alkali than by the action of alkali of the free acid. The important inference may be drawn that the active agent in promoting racemisation during the hydrolysis of an optically active ester by alcoholic alkali is the alkyloxide rather than the hydroxide.

(4) In the course of their examination of the action of alkali on the diastereoisomeric *l*-menthyl phenyl-*p*-tolylacetates, McKenzie and Miss Widdows have pointed out that, when the ester of the *d*-acid was boiled for more than an hour with a slight excess of alcoholic potassium hydroxide, the hydrolysis was incomplete. The ester recovered from this action had, however, the value $[\alpha]_D -54·7°$ in acetone, whereas the pure ester with which the experiment was conducted had $[\alpha]_D -53°$. Small as is the difference between these values, the conclusion that the original ester had undergone partial racemisation was justified. Here the racemisation causes an elevation of the optical rotatory power, inasmuch as the menthyl group in the ester is optically stable towards alkali. This observation is, so far as we are aware, the first example recorded of the catalytic racemisation of an optically active ester by alcoholic alkali. The partial conversion of *l*-menthyl *l*-diphenylsuccinate into *l*-menthyl *meso*diphenylsuccinate, as observed by Wren and Still, has also a bearing on the same problem.

Extending the observations of Wren and Still (T., 1917, **111**, 1019) on the formation of ethyl *meso*diphenylsuccinate during the

action of aqueous-alcoholic potassium hydroxide on ethyl r-diphenylsuccinate, Wren (T., 1918, **113**, 210) hydrolysed ethyl d-diphenylsuccinate with a deficiency of aqueous ethyl-alcoholic potassium hydroxide, and found that the non-hydrolysed portion consisted practically entirely of the *meso*-ester. The following result was described in the same paper. Methyl d-phenylsuccinate was treated with potassium hydroxide dissolved in slightly aqueous methyl alcohol in quantity insufficient for complete hydrolysis, and the non-hydrolysed portion was separated; this was found to be almost completely racemised. Wren's suggestion that the racemisation of methyl d-phenylsuccinate by sodium methoxide may be due to the formation of an unstable intermediate complex involves the substitution of a hydrogen atom by a sodium atom, thus :

$$
\begin{array}{cccc}
\text{CO}_2\text{Me} & \text{C}\diagup\text{OMe} & \text{CO}_2\text{Me} & \text{CO}_2\text{Me} \\
| & \| \diagdown\text{ONa} & | & | \\
\text{Ph}-\text{C}-\text{H} & \text{Ph}-\text{C} & : \text{Ph}-\text{C}-\text{H} & + \text{H}-\text{C}-\text{Ph} \\
| & | & | & | \\
\text{CH}_2\cdot\text{CO}_2\text{Me} & \text{CH}_2\cdot\text{CO}_2\text{Me} & \text{CH}_2\cdot\text{CO}_2\text{Me} & \text{CH}_2\cdot\text{CO}_2\text{Me} \\
\text{(Active.)} & \text{(Inactive.)} & \text{(Inactive.)} &
\end{array}
$$
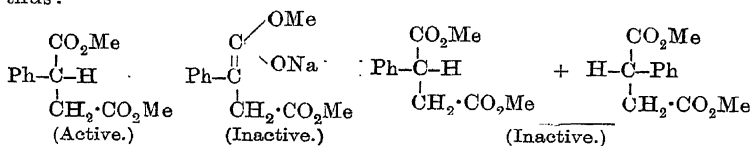
On the other hand, the interpretation of the mechanism of the racemisation of phenyl-p-tolylacetic acid by alkali, as suggested by McKenzie and Miss Widdows, is different from the above, inasmuch as it is implied that the change,

$$
\frac{\text{C}_6\text{H}_5}{\text{C}_7\text{H}_7}{>}\text{C}{<}^{\text{H}}_{\text{CO}_2\text{H}} \longrightarrow \frac{\text{C}_6\text{H}_5}{\text{C}_7\text{H}_7}{>}\text{C:C}{<}^{\text{OH}}_{\text{OH}},
$$

is not the first phase of the action, but that, in virtue of the reactivity of the carbonyl group, addition of the alkali first takes place, and the molecular rearrangement then occurs in the additive compound so formed, thus :

$$
\frac{\text{C}_6\text{H}_5}{\text{C}_7\text{H}_7}{>}\text{C}{<}^{\text{H}}_{\text{CO}_2\text{H}} \quad - \quad \frac{\text{C}_6\text{H}_5}{\text{C}_7\text{H}_7}{>}\text{C}{<}^{\text{H}}_{\underset{\underset{\text{K \ OH}}{\text{O}}}{\overset{\|}{\text{C}}-\text{OH}}}
$$

$$
\text{(Active.)} \qquad \text{(Active.)}
$$

$$
\frac{\text{C}_6\text{H}_5}{\text{C}_7\text{H}_7}{>}\text{C:C}{<}^{\text{OH}}_{\underset{\text{K \ OH}}{\text{OH}}} \qquad \frac{\text{C}_6\text{H}_5}{\text{C}_7\text{H}_7}{>}\text{C}{<}^{\text{H}}_{\text{CO}_2\text{K}} \quad + \text{H}_2\text{O}
$$

$$
\text{(Inactive.)} \qquad\qquad \text{(Inactive.)}
$$

This speculation, which implies that an additive compound is produced during the neutralisation of an organic acid by an alkali,

has an augmented interest when viewed in relationship with the recent work of Dehn and Miss Merling (*J. Amer. Chem. Soc.*, 1917, **39**, 2646). Those authors claim to have prepared a number of compounds of potassium hydroxide with various organic acids, the addition having been conducted in the presence of anhydrous ether. Thus with benzoic acid a compound was isolated which, on analysis, gave figures corresponding with the formula

$$(C_6H_5 \cdot CO_2H)_2, KOH,$$

the scheme adduced being the following:

$$2C_6H_5 \cdot CO_2H + 2KOH$$

$$\underset{\overset{\textstyle |}{\text{OH}}\quad\overset{\textstyle |}{\text{OH}}\ \ \overset{\textstyle \|}{\text{O}}}{C_6H_5 \cdot C{-}O{-}C \cdot C_6H_5}$$

$$\underset{\overset{\textstyle |}{\text{OH}}\ \ \overset{\textstyle |}{\text{OH}}\ \ \overset{\textstyle |}{\text{OH}}\ \ \overset{\textstyle |}{\text{OK}}}{C_6H_5 \cdot C{-}O{-}C \cdot C_6H_5} \qquad 2C_6H_5 \cdot CO_2K + 2H_2O$$

According to the same authors, compounds of potassium hydroxide with various esters can exist as definite entities, for example, the description of a compound consisting of molecular quantities of ethyl salicylate and potassium hydroxide is cited.

With those data at our disposal, we considered it desirable that an examination should be made in some detail of the behaviour on hydrolysis of an ester of an optically active monobasic acid of the type $R \cdot CH(OH) \cdot CO_2H$, possessing a simple structure and with a high optical rotatory power. For this purpose, ethyl *l*-mandelate, which has $[\alpha]_D -200 \cdot 2°$ in carbon disulphide solution, was selected.

First of all, the behaviour of *l*-mandelic acid towards potassium hydroxide in aqueous- and ethyl-alcoholic solutions, respectively, was examined under varied conditions of concentration and temperature. From the results recorded in table I (see experimental part), it was clear that aqueous alkali in the concentrations employed had only a very slight racemising action, even if used in considerable excess and at elevated temperature; moreover, alcoholic alkali caused racemisation, which was only slight at the ordinary temperature, but was pronounced when the alkali was in considerable excess at 70·5°.

The complete hydrolysis of ethyl *l*-mandelate was next studied, the great difference in the extent of the racemisation when effected by alcoholic alkali as contrasted with aqueous alkali being clearly indicated (see table II).

The partial hydrolysis of the ester was next examined, and the rotation taken of the non-hydrolysed ester and of the mandelic acid resulting from the potassium salt formed. It appeared that the racemisation of the ester was more pronounced than that of the

A A*

acid, and the conclusion was reached that the ester was catalytic-ally racemised. The specific rotatory power of the pure ester used was, as already stated, $[\alpha]_D -200\cdot2°$ in carbon disulphide solution. In four separate experiments conducted with alcoholic alkali under different conditions, the ester which had escaped hydrolysis and was recovered gave the values $[\alpha]_D -122\cdot1°$, $-105\cdot7°$, $-91\cdot5°$, and $-79\cdot5°$ respectively. Moreover, the effect was more noticeable at higher than at lower temperatures, and it was more extensive in alcoholic than in aqueous solutions; curiously enough, it was more marked with dilute than with concentrated alkali (see table III). The latter observation is interesting and worthy of further in-vestigation; a satisfactory interpretation would doubtless be arrived at by a comparison of the velocity of hydrolysis with the velocity of racemisation in alcoholic solutions of varying con-centrations.

Finally, ethyl l-mandelate was hydrolysed by a moderate excess of alcoholic alkali, and the optical rotatory power of the non-hydrolysed ester and of the mandelic acid obtained from the potassium salt was examined at different stages of the hydrolysis. The recovered ester gave the values $[\alpha]_D -162\cdot8°$, $-120\cdot2°$, and $-69\cdot6°$ respectively in carbon disulphide. As we anticipated, the first portions of the ester to be hydrolysed gave a highly active acid, and the activity of the non-hydrolysed ester always lagged behind that of the acid formed (see table V).

The fact is accordingly established that the action of aqueous alkali on ethyl l-mandelate under the conditions quoted in the experimental part is accompanied with very slight racemisation, whereas with alcoholic alkali under similar conditions the race-misation is pronounced. The mechanism of these two actions must obviously be different, and we suggest that with aqueous alkali the following stages may occur:

$$\begin{array}{ccc}
\text{OH} & \text{OH} & \text{OH} \\
| & | & | \\
\text{Ph–C–H} \quad (+\text{KOH}) & \text{Ph–C–H} \quad (-\text{EtOH}) & \text{Ph–C–H} \\
| & | & | \\
\text{C–OEt} & \text{C–OEt} & \text{CO}_2\text{K} \\
\end{array}$$

$$\begin{array}{ccc}
\overset{..}{\text{O}} & \text{OK} \quad \text{OH} & \\
(\text{Lævo.}) & (\text{Lævo.}) & (\text{Lævo.}) \\
\end{array}$$
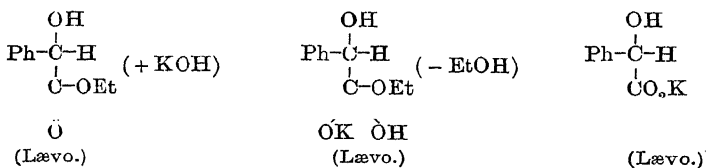
If the additive compound depicted is formed as an intermediate phase, its existence is presumably only transient, the velocity of its formation being measurably slow as compared with the velocity of its decomposition, which we would suppose to be immeasurably fast. There does not appear to be anything in such an assumption which is opposed either to the bimolecular nature of ester-hydro-

lysis or to the view held by some chemists that ionisation is the final effect instead of the initial cause of chemical reactions, and that association may precede ionisation even in aqueous solutions. A simple interpretation of this kind is not novel, recalling as it does the views advanced, for example, by H. E. Armstrong and Watson (*Proc. Roy. Soc.*, 1907, [*A*], **79**, 579) with reference to the hydrolysis of methyl acetate by hydrochloric acid and nitric acid in the presence of certain salts. Whilst it is admitted by these authors that the hydrated acid is the effective hydrolyst, the assumption is made that water acts alone and attaches itself to the carbonyl group of the ester, thus:

$$CH_3 \cdot \underset{\underset{O}{\|}}{C} \cdot O \cdot CH_3 + OH_2 \longrightarrow CH_3 \cdot \underset{\underset{OH \ OH}{\wedge}}{C} \cdot O \cdot CH_3 \longrightarrow CH_3 \cdot CO_2H + CH_3 \cdot OH.$$
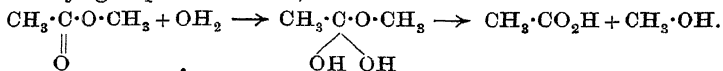
On the basis of their results on the retarding effects of the inorganic salts on the velocity of hydrolysis, the same authors go so far as to assume that the salts actually enter into association with the ester, and consequently hinder to some extent the association of ester and hydrolyst.

Now, on the representation suggested above, ethyl alcohol separates from the additive compound in such a manner that the asymmetry of the molecule is still preserved, the elimination being effected from groups which are not directly attached to the asymmetric carbon atom. If the change proceeded entirely according to this scheme, the mandelic acid resulting from the potassium salt should be the pure lævorotatory enantiomorph. In practice, however, the product is always racemised, although only slightly, and this is to be attributed mainly to the presence of a trace of potassium ethoxide formed from the alcohol eliminated. Although the equilibrated condition, $KOH + C_2H_5 \cdot OH \rightleftharpoons KO \cdot C_2H_5 + H_2O$, does not appear to have received the attention which its importance deserves, it is nevertheless certain that the quantity of ethoxide present during the hydrolysis of ethyl *l*-mandelate by aqueous alkali under the conditions examined by us can only be extremely small, sufficient, however, to induce the slight racemisation which is invariably observed. If it were feasible to select experimental conditions, of such an order that the ethyl alcohol would at the moment of its formation be removed from the sphere of action without being acted on by the potassium hydroxide, it should be possible to obtain the pure *l*-mandelic acid quite un-racemised as the product of the action of the calculated amount of aqueous alkali on the ester. It has, however, to be recognised that under certain conditions racemisation can occur even when alcohol is absent.

On the other hand, since alcoholic potassium hydroxide contains potassium ethoxide, the more pronounced racemisation effects noted with alcoholic alkali are to be attributed to this factor. Here we suppose that the first phase of the action is an additive one, and that the formation of an unsaturated, unstable complex occurs *after the additive compound has been formed,* thus:

$$
\begin{array}{ccc}
\text{OH} & \text{OH} & \text{OH} \\
\text{Ph–C–H} \quad (+\text{EtOK}) & \text{Ph–C–H} \quad (-\text{EtOH}) & \text{Ph–C} \\
\text{C–OEt} & \text{C–OEt} & \text{C} \\
\text{O} & \text{OK} \quad \text{OEt} & \text{OK} \quad \text{OEt} \\
(\text{Lævo.}) & (\text{Lævo.}) & (\text{Inactive.})
\end{array}
$$

$$
\begin{array}{ccc}
 & \text{OH} & \text{OH} \qquad \text{OH} \\
(+\text{H}_2\text{O}) \quad \text{Ph–C–H} \quad (-\text{KOH}) & \text{Ph–C–H} \quad + \quad \text{H–C–Ph} \\
\text{C–OH} & \text{C–OEt} \qquad \text{C–OEt} \\
\text{OK} \quad \text{OEt} & \text{O} \qquad\qquad \text{O} \\
(\text{Inactive.}) & (\text{Inactive.})
\end{array}
$$
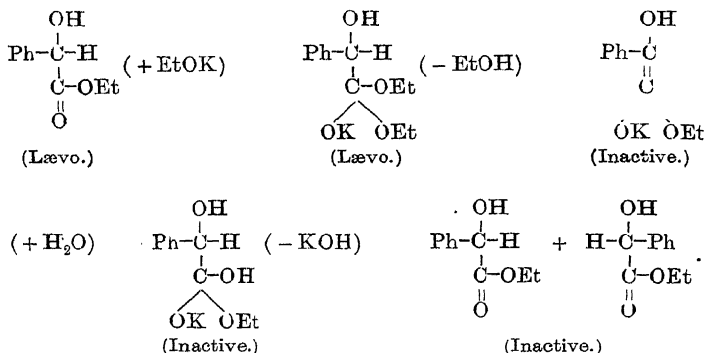
According to this picture, the asymmetry of the molecule is destroyed at the stage where the alcohol is eliminated, the ethoxide accordingly causing complete racemisation. A logical deduction would be that it should be possible to effect the complete racemisation of ethyl *l*-mandelate with potassium ethoxide if the experimental conditions could be so adjusted as to prevent the admission of potassium hydroxide into the system.

Wren's observations (T., 1918, **113**, 215) on the action of aqueous-alcoholic alkali on methyl *d*-phenylsuccinate are in harmony with the above views. With the gradual addition of water to alcoholic alkali, the amount of hydroxide will increase, whilst the amount of alkyloxide will diminish. Wren's results show clearly that the addition of water tends to check racemisation to a remarkable extent.

The fact that, when ethyl *l*-mandelate is hydrolysed by a quantity of alcoholic potassium hydroxide insufficient for complete hydrolysis the residual ester is partly racemised, would accordingly be interpreted in the following fashion. A portion of the pure ester is unattacked, whilst another portion is completely racemised by the potassium ethoxide; the ester which escapes being hydrolysed would, therefore, consist of a mixture of *d*- and *l*-esters containing an excess of the latter.

On the other hand, the following distinct reactions appear to

take place in the hydrolysis of ethyl *l*-mandelate by the calculated amount of alcoholic potassium hydroxide:

(1) The action of the aqueous potassium hydroxide present, leading to the formation of potassium *l*-mandelate practically unracemised.

(2) The catalytic total racemisation of the *l*-ester by potassium ethoxide, leading to the formation of *dl*-ester.

(3) The hydrolysis of this *dl*-ester by potassium hydroxide, leading to the formation of potassium *dl*-mandelate.

The resulting mandelic acid would therefore consist of a mixture of the *r*- and *l*-acids.

The results recorded in this paper are possibly of some importance as having a bearing on the general question of the mechanism of the hydrolysis of esters by alcoholic alkali. Let the case be considered where an ester like ethyl acetate, which does not possess an asymmetric carbon atom, is hydrolysed by an amount of alcoholic alkali insufficient for its complete hydrolysis. The non-hydrolysed ester could easily be removed, and found to be identical in every particular with the original ester. In the light of our experience, however, the conclusion would not be justified that this recovered ester was really entirely unattacked while the hydrolysis was actually in progress.

Experimental.

Action of Potassium Hydroxide on l-*Mandelic Acid.*

The acid was prepared from amygdalin, and had $[\alpha]_D -154.4°$ for $c = 2.3215$ in aqueous solution. It was heated under various conditions with an excess of potassium hydroxide dissolved in water or in ethyl alcohol. The product was finally poured into an excess of water, acidified by mineral acid, and extracted with ether. The specific rotatory power of the acid recovered from each solution was determined with water as the solvent.

Table I.

0·38 Gram of acid was taken in each experiment.

Alkali.	Conditions.	$[\alpha]_D$ of recovered acid.
30 c.c. aqueous (0·93N) ..	7 days at ord. temp.	$-151.0°$ $(c=1.14)$
,, ,, ,, ..	13 hours at 70·5°	127·4 $(c=1.42)$
30 c.c. alcoholic (0·93N) ..	7 days at ord. temp.	146·6 $(c=0.86)$
,, ,, ,, ..	13 hours at 70·5°	61·2 $(c=1.79)$
30 c.c. aqueous (0·1105N)	15 days at ord. temp.	152·3 $(c=1.3)$
,, ,, ,,	20 hours at 70·5°	148·6 $(c=1.76)$
30 c.c. alcoholic (0·1105N)	15 days at ord. temp.	151·7 $(c=1.52)$
,, ,, ,,	20 hours at 70·5°	145·5 $(c=1.19)$

For the neutralisation of 0·38 gram of acid, 22·6 c.c. of 0·1105N-alkali are required. When a slight excess of alkali of this concentration was employed, there was still racemisation; the effect of raising the temperature is, however, clearly indicated, as also is the greater racemising effect of the alcoholic as contrasted with the aqueous alkali. The effects of the more concentrated alkali (0·93N) were more pronounced. Although the value $-146·6°$ obtained from the third experiment quoted in the above table is not far removed from that of the optically pure l-mandelic acid, the racemisation which occurred when the alcoholic solution was kept at the ordinary temperature and submitted to polarimetric examination at intervals was observed quite clearly, the α_D falling from $-1·21°$ to $-1·08°$ ($l=1$) after seven days. At 70·5°, the initial value for α_D was $-2·42°$ ($l=2$); after one hour α_D was $-2·15°$, and after three hours $-1·92°$, whilst the acid recovered after the action had proceeded for thirteen hours had a value so low as $[\alpha]_D -61·2°$. It must, of course, be noted that the alkali in this experiment was present in considerable excess. On the other hand, with aqueous alkali (0·93N), the initial value for α_D was $-2·89°$ ($l=2$); after three hours at 70·5°, the value had fallen to $-2·80°$, and after thirteen hours to $-2·45°$, whilst the recovered acid had $[\alpha]_D -127·4°$ after the action had been in progress for thirteen hours.

With regard to the conditions, the experiments quoted in the table are strictly comparable, as they were performed simultaneously.

Complete Hydrolysis of Ethyl l-Mandelate by Potassium Hydroxide.

The ester was prepared by esterifying the acid with ethyl alcohol and sulphuric acid. Its rotation was determined in carbon disulphide:

$$l=2, \ c=2·0155, \ \alpha_D^{14} -8·07°, \ [\alpha]_D^{14} -200·2°.$$

This value is higher than that quoted by Walden (*Zeitsch. physikal. Chem.*, 1895, **17**, 708), who gives $[\alpha]_D -180°$ in carbon disulphide for $c=2·5$.

TABLE II.

Ester, grams.	Alkali.	Alkali required.	Conditions.	$[\alpha]_D$ of recovered acid.
0·697	35·5 c.c. alcoholic (0·1105N).	35·0 c.c.	3 days at ord. temp.	$-86\cdot0°$ $(c=1\cdot9)$
0·697	35·5 c.c. alcoholic (0·1105N).	,,	6 hours at 70°	$74\cdot5$ $(c=2\cdot32)$
0·789	80 c.c. alcoholic (0·1105N).	39·6	5 days at ord. temp.	$93\cdot7$ $(c=2\cdot05)$
0·789	80 c.c. alcoholic (0·1105N).	,,	6 hours at 70°	$80\cdot6$ $(c=2\cdot62)$
1·0639	6·6 c.c. alcoholic (0·93N).	6·35	20 hours at ord. temp.	$112\cdot4$ $(c=3\cdot16)$
1·0639	6·6 c.c. alcoholic (0·93N).	,,	3 hours at 70°	$105\cdot1$ $(c=3\cdot07)$
0·721	10 c.c. alcoholic (0·93N).	4·3	2 days at ord. temp.	$118\cdot4$ $(c=2\cdot05)$
2·0516	10 c.c. alcoholic (2·18N).	5·2	1¾ hours at ord. temp.	$124\cdot1$ $(c=2\cdot14)$
0·5192	27 c.c. aqueous (0·1105N).	26·1	4 days at ord. temp.	$149\cdot4$ $(c=1\cdot8)$
0·5893	30·5 c.c. aqueous (0·1105N).	29·6	6 hours at 70°	$152\cdot2$ $(c=1\cdot93)$
0·9408	6 c.c. aqueous (0·93N).	5·6	1 day at ord. temp.	$147\cdot3$ $(c=2\cdot99)$
0·9008	5·8 c.c. aqueous (0·93N).	5·4	4 hours at 70°	$146\cdot5$ $(c=3\cdot24)$
0·6785	8·1 c.c. aqueous (0·93N).	4·0	2½ hours at 70°	$144\cdot8$ $(c=2\cdot06)$

Experiments with excess of hot concentrated alcoholic alkali were not performed, since the product would have been appreciably racemised by the alkali after the completion of the hydrolysis, and the value for the specific rotation would have varied according to the duration of heating.

Our thanks are due to Mr. Henry Wood, who in 1906 carried out the following experiments with the methyl and propyl esters of *l*-mandelic acid. A mixture of 3 grams of methyl *l*-mandelate and 50 c.c. of an aqueous solution of potassium hydroxide (1·114 grams, calculated 1·014 grams) was maintained at the ordinary temperature for seven days. The acid obtained gave the value $[\alpha]_D - 153\cdot9°$ for $c = 1\cdot99$. An experiment conducted under similar conditions with 3 grams of the ester and 48·5 c.c. of alcoholic potassium hydroxide (1·016 grams) gave an acid with $[\alpha]_D - 115\cdot9°$. These results showed the difference between the behaviour of aqueous and alcoholic alkali. When propyl-*l*-mandelate was hydrolysed with a slight excess of aqueous alkali at the ordinary temperature, the acid recovered gave the value $[\alpha]_D - 149\cdot4°$; the behaviour of this ester towards alcoholic alkali was not examined at the time.

Partial Hydrolysis of Ethyl l-*Mandelate.*

(1) *With Ethyl-alcoholic Potassium Hydroxide* ($0\cdot1105N$).—
Ester, $3\cdot7273$ grams; 94 c.c. of alkali (calculated $187\cdot3$ c.c.).   The
solution was divided into two equal parts: (a) *At the ordinary
temperature for forty-eight hours.*—The alcohol was removed from
the neutral solution by evaporation, the residue added to water,
and the non-hydrolysed ester extracted with ether and dried; its
rotation determined in carbon disulphide solution was $[\alpha]_D - 105\cdot7°$
for $c = 2\cdot19$.   The mandelic acid was obtained from the potassium
salt in the usual manner, and its rotation determined in aqueous
solution was $[\alpha]_D - 119\cdot9°$ for $c = 3\cdot03$.   (b) *At 70° for four hours.*—
Recovered ester, $[\alpha]_D - 79\cdot5°$ for $c = 4\cdot69$; acid, $[\alpha]_D - 110\cdot9°$ for
$c = 3\cdot57$.

(2) *With Ethyl-alcoholic Potassium Hydroxide* ($0\cdot93N$).—Ester,
$3\cdot4658$ grams; 10 c.c. of alkali (calculated $20\cdot7$ c.c.).   The solu-
tion was divided into two equal parts: (a) *At the ordinary
temperature for twenty-four hours.*—Recovered ester, $[\alpha]_D - 122\cdot1°$
for $c = 3\cdot15$; acid, $[\alpha]_D - 131\cdot3°$ for $c = 3\cdot37$.   (b) *At 70° for six
hours.*—Recovered ester, $[\alpha]_D - 91\cdot5°$ for $c = 2\cdot13$; acid,
$[\alpha]_D - 122\cdot1°$ for $c = 2\cdot31$.

(3) *With Aqueous Potassium Hydroxide* ($0\cdot93N$).—Ester,
$3\cdot4156$ grams; 10 c.c. of alkali (calculated $20\cdot4$ c.c.).   *At the
ordinary temperature for three days.*—Recovered ester,
$[\alpha]_D - 181\cdot8°$ for $c = 4\cdot82$; acid, $[\alpha]_D - 152\cdot2°$ for $c = 2\cdot02$.

These results are contrasted in the following table.

TABLE III.

Alkali.	t.	Ester hydro-lysed, per cent.	$[\alpha]_D$ of residual ester.	$[\alpha]_D$ of acid.	Race-misation of ester, per cent.	Race-misation of acid, per cent.
Alcoholic $0\cdot1105N$	Ord.	$50\cdot2$	$-105\cdot7°$	$-119\cdot9°$	$47\cdot2$	$22\cdot3$
,, ,,	70°	,,	$79\cdot5$	$110\cdot9$	$60\cdot3$	$28\cdot2$
Alcoholic $0\cdot93N$	Ord.	$48\cdot3$	$122\cdot1$	$131\cdot3$	$39\cdot0$	$15\cdot0$
,, ,,	70°	,,	$91\cdot5$	$122\cdot1$	$54\cdot3$	$20\cdot9$
Aqueous, $0\cdot93N$	Ord.	$49\cdot0$	$181\cdot8$	$152\cdot2$	$9\cdot2$	$1\cdot4$

*Examination at Different Stages during the Complete Hydrolysis
of Ethyl* l-*Mandelate by Alcoholic Alkali.*

The ethyl-alcoholic potassium hydroxide used was $0\cdot202N$.   Six
grams of the ester were dissolved rapidly at the ordinary tempera-
ture by shaking with 205 c.c. of alkali (calculated 165 c.c.).   At
intervals, 50 c.c. of the solution were withdrawn and run into a

slight excess of standard sulphuric acid, the solution being then titrated with standard alkali. In each case, the alcohol was removed by heating, and the ester and mandelic acid in the residue were separated as usual. .

TABLE IV.

Interval.	Solution withdrawn.	Sulphuric acid, 0·998N.	0·202N-alkali required for excess of acid.
7 minutes	50 c.c.	10 c.c.	11·0 c.c.
25 ,,			23·0 ,,
65 ,,			33·9 ,,
1269 ,,			40·1 ,,

In table V, the specific rotatory power of the mandelic acid was determined in ethyl-alcoholic solution, the acid from which the ethyl l-mandelate was prepared having $[\alpha]_D$ $-152°$ for $c=1·671$ in ethyl alcohol.

TABLE V.

...tion.	Ester hydro-lysed, per cent.	$[\alpha]_D$ of ester recovered.	$[\alpha]_D$ of acid.	Ester racemised, per cent.	Acid racemised, per cent.
1	28	$-162·8°(c=2·45)$	$-138·2°(c=1·1)$	18·7	9·1
2	58	120·2 $(c=1·46)$	119·0 $(c=1·02)$	40·0	21·7
3	84	69·6 $(c=0·52)$	104·3 $(c=2·85)$	65·2	31·4
4	100	—	96·3 $(c=2·69)$	—	36·6

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LI.—*The Potential of a Nitrogen Electrode.*

By FRANCIS LAWRY USHER and RAMAVENKATASUBBIER VENKATESWARAN.

THE decomposition potential of a normal solution of hydrazoic acid has been found by Le Blanc to be 1·29 volts, and this acid therefore resembles the halogen acids (except hydrofluoric) in furnishing at the anode an electromotively active substance the potential of which is lower than that of oxygen. The substance in question has been presumed to be ordinary nitrogen, so that it should be possible to construct a nitrogen electrode similar to a chlorine or a hydrogen electrode, and to measure its potential in a solution containing N'_3 ions. An attempt which we have made to do this

has led to some interesting results, which leave little doubt that the substance set free at the anode in the electrolysis of azide solutions is not ordinary nitrogen, but an active form of it. Some purely chemical evidence in support of this conclusion was obtained by one of us in 1914, and it is proposed to resume these experiments as soon as circumstances permit; they are at present too incomplete for publication.

EXPERIMENTAL.

The $E.M.F.$ of the combination $N/10$-calomel $|N/100$-KCl$|$ $N/100$-NaN$_3|$N$_2$Pt was measured at 30°, the nitrogen employed being carefully freed from oxygen and oxides. The nitrogen electrode was about 0·4 volt negative to the calomel, and therefore slightly negative to hydrogen, a result which is clearly incompatible with the assumption that the nitrogen furnishes N$'_3$ ions reversibly. It was, in fact, proved that the observed potential was unaffected by the presence of nitrogen. The attempt was repeated with several different kinds of electrode, but always with the same negative result.

Since the nitrogen liberated at the anode during the electrolysis of azide solutions is electromotively active, as shown by the existence of a definite decomposition voltage, it appeared probable that at the moment of its liberation it was different from, but was very rapidly converted into, ordinary nitrogen. It was therefore decided to polarise a platinum wire anodically in an azide solution with a definite $E.M.F.$ in slight excess of the decomposition voltage, and to measure its potential, which would be slightly higher than the true potential corresponding with the reversible change N$'_3$ $\rightleftharpoons$ active nitrogen. The electrolytic cell was made of paraffined teakwood divided into three compartments by parchment paper diaphragms, the three compartments containing N-sodium azide, with some hydrazoic acid added to the middle compartment in order to neutralise any ammonia formed by reduction at the cathode. The potential of the anode was measured against a $N/10$-calomel electrode at the ordinary temperature (25—26°). The results read from the smoothed curves are shown in the following table. In Series I, about 5 cm. of platinum wire 0·5 mm. thick were used, in Series II about 2 mm. of the same wire, and in Series III a short point of very fine wire, the metal being well platinised in every case.

Applied $E.M.F$ Volts.	Potential of anode against $N/10$-calomel		
	I.	II.	III.
1·20	0·690	0·760	0·788
1·30	0·698	0·770	0·800
1·40	0·704	0·782	0·813
1·50	0·712	0·797	0·829
1·60	0·722	0·812	0·843
1·70	0·732	0·830	0·861
1·80	0·743	0·848	0·880
1·90	0·754	0·873	0·904

Although the combination was so arranged that the potentials at the liquid junctions could be calculated after determining the transport number for sodium azide, it was unnecessary to do this, because, as is evident from the above table, a constant value for the potential of the nitrogen electrode was not obtained at any applied voltage. Its behaviour appears to be normal so far as the effect of increasing voltage is concerned, but depends on the size of the anode, that is, on the current density. The current flowing in the primary circuit was at all times sufficient to cause a brisk evolution of gas, so that the results cannot be attributed to want of saturation. With a view to investigate the relation between the potential and the current density, a series of measurements was made with varying but known current densities at a constant decomposing voltage.* The arrangement shown diagrammatically in the accompanying figure was used. The solution of N-sodium azide, slightly acidified with hydrazoic acid, was contained in a tall U-tube with a side branch for the calomel electrode (E). The electrodes (AC) consisted of platinised platinum disks sealed into glass tubes which passed through corks, and could be moved up or down. The U-tube was tilted when in use in order to prevent an accumulation of gas under the disks. The electrolysing current was furnished by a battery (B), and passed through an adjustable low resistance (W), a resistance box (R), and the solution in the U-tube. SS are two paraffin block switches of which the terminals d and g were connected to a potentiometer (P), the other connexions being as shown in the diagram. In taking a series of readings, the circuit was first closed, e was connected to g, and a to d. Plugs were then taken out of the resistance box until the potential difference across the U-tube was approximately 1·31 volts (chosen as being slightly in excess of the decomposition voltage), and the rheostat (W) was then adjusted so that that figure was exactly attained. The second measurement was that of the fall of potential across the resistance box, and the third gave the $E.M.F.$ of the combination nitrogen—

* Keys, standard cell, and a buffer solution between the U-tube and calomel electrode are not shown.

calomel. The current flowing through the solution was known from the second measurement, which gave the fall of potential across a known resistance, and from this the current density was calculated, the area of the anode being always the same, namely, 0·65 sq. cm. By altering the position of the electrodes, the resistance of the solution could be varied, and therefore also the current density.

It was noticed that when the platinised electrodes were immersed in the solution, a slow evolution of nitrogen occurred even when no current was passed. This could not have been due to occluded
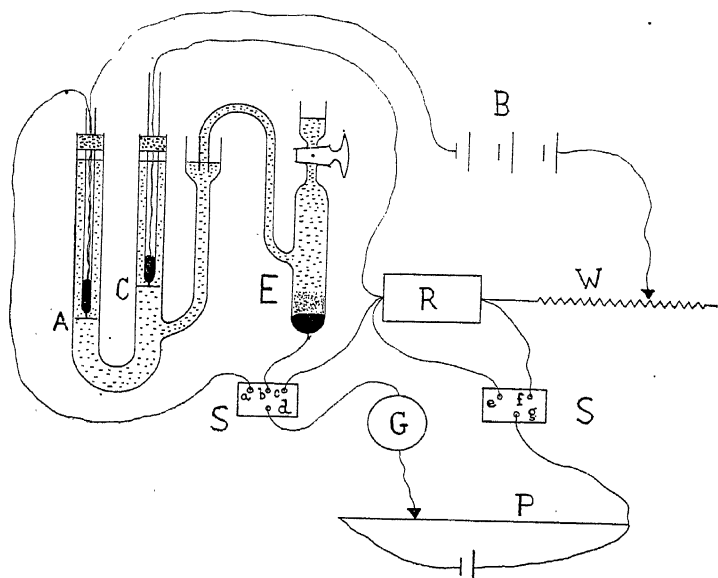
chlorine derived from the platinising liquid, since it took place after soaking the electrodes in ferrous sulphate solution and washing them thoroughly, but was probably due to catalytic decomposition by the platinum black. Shortly after this observation was made, we found that the phenomenon had already been studied by Oliveri-Mandalà (*Gazzetta*, 1916, **46**, ii, 137). The platinum apparently became " poisoned " after the evolution had proceeded for some time, and nitrogen ceased to be given off after the first series of readings had been taken. The following table shows the results obtained. The current density at the anode (C.D.) is given

in microamperes per sq. cm., and the $E.M.F.$ of the combination volts.

I.		II.		III.		IV.	
C.D.	$E.M.F.$	C.D.	$E.M.F.$	C.D.	$E.M.F.$	C.D.	$E.M.F$
4707	0·446	4070	0·493	3659	0·508	3768	0·494
4838	0·468	4244	0·506	3738	0·524	3816	0·518
4975	0·482	4285	0·516	3831	0·542	3847	0·545
5136	0·497	4377	0·528	3893	0·558	3893	0·561
5444	0·520	4541	0·540	4019	0·577	3988	0·587
5741	0·541	4670	0·552	4112	0·593	4051	0·617
6131	0·564	4868	0·561	4237	0·608	4144	0·652
		4992	0·581	4364	0·629		
		5157	0·590				
		5362	0·615				
		5546	0·635				

If the above figures are plotted on a curve, it is seen that, as one would expect, the rate of increase of potential with current density diminishes as the latter increases. Since the potential is a measure of the concentration of the electromotively active substance in the electrode (assuming the solution to remain unaltered), it is evident that the latter is unsaturated even when nitrogen is being evolved freely, and one can only explain this behaviour by assuming that the N'_3 ions furnish an active form of nitrogen on discharge, and that this is rapidly converted into ordinary nitrogen, probably catalytically by the platinum.

It has been shown in other instances that the velocity of reaction between a gas and a solid is proportional to the partial pressure of the gas. In the present case, the rate of formation of active nitrogen must be proportional to the current density, and its rate of decomposition may be considered proportional to its partial pressure, that is, to its concentration, of which the potential is a known function. If, therefore, the measurements correspond with a state of equilibrium (which they probably do, since the potential shows no variation so long as the current density remains constant),* we obtain the relation : rate of formation of active nitrogen $= k_1 D =$ rate of decomposition $= k_2 C$, where D is the current density and C the concentration of active nitrogen. If P is the measured $E.M.F.$, we get † $P = a + b \log D$, where a and b are constants. The following table shows the experimental values of the $E.M.F.$ in Series II, the values read from a smoothed curve drawn through

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* In the four series of readings given, the actual values of the potential in the different series are not the same for a given current density. This variation is due to differences in the solutions, and is not observed in a solution of definite composition.

† By substituting $C = k_1 D / k_2$ in the expression $P = k + b \log c$, and collecting the constant terms.

the figures enclosed in brackets, and the values calculated by means of this expression :

E.M.F.

C.D.	Measured.	Read from smoothed curve.	Calculated
(4070)	(0·493)	(0·493)	(0·493)
4244	0·506	0·512	0·512
4285	0·516	0·516	0·516
4377	0.528	0·526	0·525
4541	0·540	0·542	0·542
4670	0·552	0·554	0·554
4818	0·561	0·568	0·568
4992	0·581	0·584	0·584
5157	0·590	0·598	0·598
(5362)	(0·615)	(0·615)	(0·615)
5546	0·635	0·630	0·630

The agreement between the observed and calculated figures is satisfactory, and probably indicates that the assumptions made are in the main correct. It is interesting to note that the above expression does not fit the curve obtained in Series I, where the solution was being decomposed catalytically during the observations, but that if a third constant (representing a constant additional supply of active nitrogen) is introduced, the agreement becomes good.

An attempt was made to obtain some idea of the rate at which the active nitrogen is decomposed in contact with the electrode. An azide solution was electrolysed in such a way that the gas accumulated in bubbles under the anode. On breaking the decomposing current, the potential fell at first so rapidly that it could not be followed, and dwindled to zero in about thirty seconds. A similar experiment with chlorine showed that the potential fell by 0·2 volt in twenty minutes, and a hydrogen electrode by 0·06 volt in the same time, so that the result with nitrogen cannot be explained by diffusion.

The only reference to any peculiarity in the chemical properties of the nitrogen obtained by electrolysing an azide appears to be in a paper by Browne and Lundell (*J. Amer. Chem. Soc.*, 1909, **31**, 435), who electrolysed a solution of potassium azide in anhydrous azoimide at −78°, and, on the occasions when their apparatus was not shattered, observed that the gas evolved at the anode attacked mercury. Apparently, therefore, the active nitrogen is much less rapidly decomposed at a low temperature.

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LII.—*A Chemical Investigation of Banded Bituminous Coal. Studies in the Composition of Coal.**

By FREDERICK VINCENT TIDESWELL and RICHARD VERNON WHEELER.

IT is, and has been since pit-coal first became an article of daily use, a matter of common observation that any lump of bituminous coal taken haphazard is almost certain to exhibit, in a more or less marked degree, differences in the texture of its surface which give it a banded appearance, the bands being alternately dull and bright.

The subject of the banded appearance of bituminous coal has recently been treated in a more exact manner than heretofore by Stopes (*Proc. Roy. Soc.*, 1919, [*B*], **90**, 470), whose observations can be briefly summarised as follows.

She distinguishes, not merely "dull" and "bright" bands, but four distinctive portions forming the mass of an ordinary bituminous coal. The four portions can be recognised and separated from each other both macroscopically and microscopically in thin sections. These four ingredients were provisionally named by Stopes:

    (i) Fusain.   The equivalent of "mother-of-coal," "mineral-charcoal," etc., of various authors.

    (ii) Durain.   The equivalent of "dull" hard coal of various authors; the "Mattkohle" of the Germans.

    (iii) Clarain. ⎰ Together the equivalent of "bright" or "glance" coal of
    (iv) Vitrain. ⎱   various authors; the "Glanzekohle" of the Germans.

These show various differences in character, and, in particular, markedly distinct microscopical features.

Microscopical and palæobotanical study has thus been able to distinguish between four visible ingredients in banded bituminous coal, and to ascribe to each a character essentially different from the others as regards the appearance and probable nature of the materials of which it is composed. As a corollary to this work, we have undertaken to determine to what extent, or if at all, the four ingredients differ amongst themselves in their chemical nature as ascertained by ordinary methods.

So far as we are aware, the only previous detailed attempt to relate the texture with the chemical composition of a coal is that

* The work by Dr. M. C. Stopes, the reference to which is given below, forms No. 1 of this series of researches.

by Grout (*Econ. Geol.*, 1911, **6**, 449), who made a careful study of selected parts of a black lignite or sub-bituminous coal from Gorham Mine, Marshall, Colorado. Several references are to be found, it is true, to the difference in composition between a sample of "mother-of-coal" (fusain) and the coal with which it was associated; and there has been a tendency on the part of some writers to confuse fusain, which may occur in bands or layers, but is just as often present in coal in numerous very small pockets, with "dull" or "matt" coal (durain) (see, for example, Strahan and Pollard, *Mem. Geol. Surv. Engl. Wales*, 1915, **6**, 91).

We do not propose to discuss the reason for the gross difference that undoubtedly exists between the chemical composition of fusain and that of coal, but to reserve such a discussion for a future memoir, since it belongs more properly to a disquisition on the mode of formation of the coal conglomerate. Our immediate concern is with the more subtle differences in composition that can be presumed to be correlated with the characteristic appearances of vitrain, clarain, and durain.

The coal chosen for this research was, for obvious reasons, one of those used by Dr. Marie Stopes for her investigations, namely, the Thick Coal, Hamstead Colliery. We are indebted to her for volunteering the task—a laborious one requiring much care—of providing supplies of each macroscopically distinct ingredient, free from the others, sufficient for chemical examination. The total supply was obtained from blocks of coal collected within a few cm. of each other in the same portion of the seam.

The fusain was obtained as a powder by scraping lightly with a knife at such cleavage surfaces as had wedges of the material on them. The durain was obtained as small blocks or broken bands by splitting off from it all bright streaks. To obtain the durain reasonably pure, it was necessary to split the coal considerably; although preponderatingly dull in appearance, a few bright streaks of hair-like fineness remained in it. In contrast to the brittle, powdery fusain, the durain is firm and hard.

Clarain preponderated in the sample. It is throughout banded finely with rather brighter and rather duller portions, but in general it has a subdued surface lustre when viewed broken at right angles to the bedding plane, which is distinct from the matt surface of the durain.

Vitrain is a conspicuous feature in a block of this coal. It was separated as small splints and cubes through the ready breaking up of its layers. The vitrain runs in horizontally extended bands varying from 1 to 6 mm. in thickness. Unlike the clarain, a single band does not show banding within itself, but the face at right

angles to the bedding plane is uniformly and brilliantly glossy, and instead of the usual cleavage the fracture tends to be conchoidal.

The methods of chemical investigation employed for each of the four ingredients have been: proximate and ultimate analysis; the action of solvents and of reagents; and destructive distillation in a vacuum, with examination of the gaseous and liquid products. A tabulation of the results obtained, so far as they admit of tabulation, is given later. Some description is first required of the different operations, further details of which are given in the experimental portion of the paper.

The Action of Solvents.—Extractions were made in Soxhlet fat-extraction apparatus, using from 1 to 10 grams of material ground so as to pass through a 200×200 mesh sieve.

(1) *Pyridine:*

	Vitrain.	Clarain.	Durain.	Fusain.
Extract, per cent. on ash-free, dry coal	34·4	27·2	21·6	10·1
Colour of solution	Dark red.	Dark red.	Brownish-red.	Brown.

(2) *Chloroform Extraction of Pyridine Extract.*—One gram of each of the dried extracts of vitrain, clarain, and durain was extracted with chloroform during two days. Extraction appeared to be complete after twelve hours. The percentage of the pyridine extract soluble in chloroform was with vitrain 27, with clarain 30, and with durain 40.

From these results, the percentages of α-, β-, and γ-compounds present in the coal (see Stopes and Wheeler, "Monograph on the Constitution of Coal," 1918) can be calculated as follows:

	Vitrain.	Clarain.	Durain.
α-Compounds (insoluble in pyridine)...	65·8	72·8	78·4
β-Compounds (soluble in pyridine, but insoluble in chloroform)	25·0	19·0	13·0
γ-Compounds (soluble in both pyridine and chloroform)	9·2	8·2	8·6

Samples of vitrain and durain were extracted direct with chloroform and with ethyl alcohol; the percentages extracted are recorded in table V.

The Action of Reagents. (1) *Alcoholic Potassium Hydroxide.*—This reagent has been used by previous workers to determine the quantity of ulmin compounds present in a coal. The substances removed are no doubt ulmin compounds, but all such compounds are not necessarily soluble in aqueous or alcoholic potassium hydroxide (Stopes and Wheeler, *loc. cit.*); it is better, therefore, simply to record the fact that a certain portion of a coal is soluble in the

reagent, without attempting to draw any conclusion therefrom as to the total percentage of ulmin compounds present.

A modification of Hart's method of treatment (*Chem. Zeit.*, 1907, **31**, 640), in which the reagent is maintained at 80°, was used in the first instance, the results being:

	Vitrain.	Clarain.	Durain.
Soluble in hot alcoholic potassium hydroxide; per cent. on ash-free, dry coal	6·1	5·4	3·8

Stopes had observed that in the cold this reagent seemed to have a peculiar effect on vitrain, causing small lumps to "acquire the consistency of hard cheese or soap," so that thin flakes could be cut from it with a razor, whilst in untreated coal vitrain is hard and resistant to a cutting edge. It seemed desirable, therefore, to determine whether prolonged treatment of the powdered coals in the cold would result in greater quantities passing into solution. The percentages removed after eight weeks of such treatment were:

Vitrain.	Clarain.	Durain.
5·7	5·2	3·6

The softening or loosening action of the alkali observed by Stopes would thus appear to be caused by the removal of some binding material from the coal conglomerate; the ulmin compounds have been credited with a binding or cementing action.

(2) *Iodine.*—The absorption of iodine by coal may be regarded as giving an approximate measure of the proportion of unsaturated compounds present.

Before treating the four ingredients of banded coal, preliminary trials were made with other coals to determine the conditions of test most likely to yield accurate comparative results These trials showed that iodine absorption by coal is very slow and may continue for a long time. It was, in fact, found to be impracticable to determine the maximum amount of iodine that can be absorbed by coal, for the absorption varied with the conditions, and more particularly with the length of duration of test. For example, Wijs' solution (iodine chloride in solution in glacial acetic acid), although causing about four times the absorption given by aqueous iodine, yet did not appear to be within measurable distance of giving a final value after twelve hours.

In recording the results that follow, it is necessary to distinguish between "permanent" and "temporary" absorption of iodine (see p. 635). The results given are strictly comparative, each of the four components of banded coal being treated under identical conditions.

TABLE I.

Iodine Absorbed per cent. by Weight on Ash-free, Dry Coal.

Duration of treatment.	Temporary. (Released on keeping.)				Permanent.			
Hours.	Vitrain.	Clarain.	Durain.	Fusain.	Vitrain.	Clarain.	Durain.	Fusain.
1.	6·4	7·6	4·1	0·7	8·6	6·9	6·8	2·1
3·	7·9	8·3	5·5	0·7	14·3	11·8	12·3	3·6
6.	9·3	9·7	6·8	1·4	16·5	16·0	13·0	2·9
24.	10·7	10·4	8·9	2·1	22·8	23·6	17·8	4·3

These results were obtained with aqueous iodine ($N/10$ in potassium iodide solution). With Wijs' solution, the following quantities of iodine, calculated as percentages on the ash-free, dry coals, were absorbed during six hours:

Temporary.				Permanent.			
Vitrain.	Clarain.	Durain.	Fusain.	Vitrain.	Clarain.	Durain.	Fusain.
18·6	20·8	17·1	8·6	67·9	63·2	51·3	4·3

Destructive Distillation. Gaseous Products.—The procedure adopted for the examination of the gaseous products was that of fractional distillation in a vacuum. In this manner, the ranges of temperature over which decompositions occurred, with the production of one or other of the usual constituents of coal-gas in predominant quantity, became manifest. With each of the four ingredients of banded coal, decomposition, as evinced by the evolution of gases in any quantity, did not become marked until a temperature of about 350° was reached, although slight decomposition occurred with each at a temperature of 300°. At 200°, with all except fusain, a trace of gas was evolved, together with a little liquid having an odour of light petroleum.

The tabulated results of the distillations are as follow:

TABLE II.

Vitrain.

Temperature	0–300	300–350	350–400	400–450	450–500	500–550	550–600°
Vol. of gas at N.T.P. evolved per gram of coal, c.c.	5·0	6·2	22·5	25·9	37·4	49·8	52·0
Analysis, per cent.							
$C_6H_6 + C_nH_{2n}$	8·3	12·0	8·8	2·2	0·7	nil	nil
$CO_2 + H_2S$	58·3	20·4	7·3	3·3	2·3	1·1	1·1
O_2	0·5	0·4	nil	nil	nil	nil	nil
C_2H_4	1·8	4·8	4·8	1·9	0·4	nil	nil
CO	21·7	20·8	14·8	15·1	15·0	11·3	12·1
H_2	—	2·8	9·7	35·2	59·8	80·1	82·2
C_nH_{2n+2}	8·0	38·8	55·1	42·3	21·8	7·5	4·6
Ratio C/A on explosion for paraffins	1·50	1·56	1·80	1·85	1·95	2·00	2·00

TABLE II. (*continued*).

Clarain.

Temperature	0–300	300–350	350–400	400–450	450–500	500–550	550–600°
Vol. of gas at N.T.P. evolved per gram of coal, c.c.	4·5	5·4	19·8	23·0	35·0	35·7	50·0
Analysis, per cent.							
$C_6H_6 + C_nH_{2n}$	9·0	10·0	9·0	2·3	0·9	nil	nil
$CO_2 + H_2S$	58·5	24·5	10·6	6·3	4·0	1·4	1·3
O_2	0·5	0·3	trace	nil	nil	nil	nil
C_2H_4	1·5	4·2	4·6	2·0	0·3	nil	nil
CO	21·0	21·6	14·4	14·5	14·0	11·9	12·3
H_2	—	3·0	9·3	33·0	58·5	76·0	80·0
C_nH_{2n+2}	7·5	34·4	52·1	41·9	22·3	10·0	6·4
Ratio C/A on explosion for paraffins	1·52	1·60	1·71	1·80	1·90	2·00	2·00

Durain.

Temperature	0–300	300–350	350–400	400–450	450–500	500–550	550–600°
Vol. of gas at N.T.P. evolved per gram of coal, c.c.	3·55	5·4	15·4	18·9	31·0	30·0	35·8
Analysis, per cent.							
$C_6H_6 + C_nH_{2n}$	11·6	14·4	11·7	2·5	1·8	nil	nil
$CO_2 + H_2S$	58·7	28·3	13·8	9·2	6·7	6·2	2·0
O_2	0·6	0·4	0·1	nil	nil	nil	nil
C_2H_4	1·0	3·3	4·3	2·1	0·3	nil	nil
CO	19·3	19·1	12·4	13·5	15·0	16·4	12·6
H_2	nil	3·0	7·7	32·1	56·6	62·7	77·0
C_nH_{2n+2}	7·3	29·8	50·0	40·6	19·6	14·7	8·4
Ratio C/A on explosion for paraffins	1·40	1·45	1·70	1·85	1·95	2·00	2·00

Fusain.

Temperature	0–300	300–350	350–400	400–450	450–500	500–550	550–600°
Vol. of gas at N.T.P. evolved per gram of coal, c.c.	1·8	2·0	7·5	12·0	17·5	22·0	35·0
Analysis, per cent.							
$C_6H_6 + C_nH_{2n}$	11·5	8·9	7·5	2·8	1·8	0·7	nil
$CO_2 + H_2S$	56·4	38·0	20·0	11·4	8·2	6·4	3·8
O_2	nil	nil	nil	nil	nil	nil	nil
C_2H_4	2·3	3·5	3·0	2·2	0·7	0·2	nil
CO	20·8	20·1	16·0	15·8	18·1	17·2	13·3
....	nil	2·4	10·6	22·6	38·4	56·7	73·9
C_nH_{2n+2}	3·0	23·0	42·3	45·2	32·8	18·5	9·0
Ratio C/A on explosion for paraffins	1·25	1·42	1·60	1·82	1·90	2·00	2·00

In Figs. 1 and 2 are shown the volumes of individual gases plotted against the temperatures at which they were evolved.   The

FIG. 1.

Temperature.
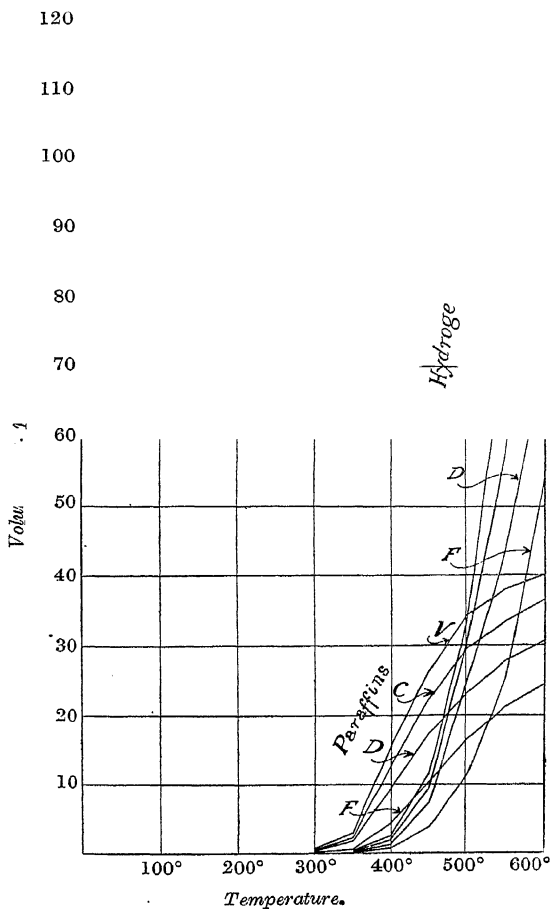
curves thus obtained show clearly the various stages of decomposition of the coal.

Destructive   Distillation.   Primary   Liquid   Products.—Only vitrain and durain were submitted to destructive distillation with

a view to examine the primary liquid products. Of fusain, an insufficient quantity was obtainable, whilst it seemed probable that the behaviour of clarain could be deduced from that of the other two components of banded coal, which would, at all events, afford the maximum degree of contrast. The records of the distillations are as follow.

Vitrain. May 31st, 1918.—The apparatus (see p. 636) having been exhausted of air, heating was begun at 2.0 p.m., the temperature being raised slowly to 100°. This temperature was main-

Fig. 2.
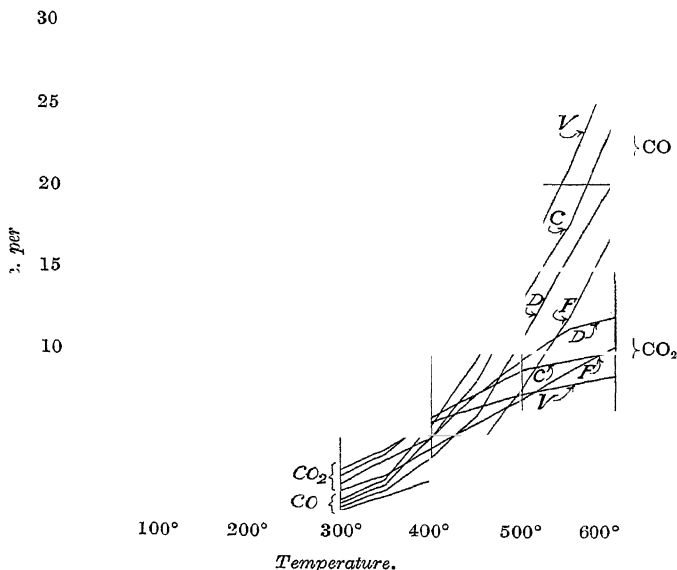
Temperature.

tained until noon on June 3rd. Water collected in the cooled receivers. *June 3rd.*—The temperature was raised gradually to 300°. Water and a little gas were evolved as the temperature increased. Oils began to appear at 300°. *June 4th.*—Increase of temperature was continued very slowly from 300° in order to determine the point at which active decomposition began. This was found to lie between 350° and 360°, over which range there was a rapid evolution of gas, water, and oils. Throughout the day the temperature was raised slowly to 400°. Viscid red oils began to appear at 390°, and their quantity increased with increased

temperature up to 455° (June 5th). *June 5th—7th.*—The temperature was raised, in stages of 25°, up to 550°. A rapid evolution of gas occurred at each successive increment of temperature, but there was no further appreciable production of oil or tar above 460°.

Durain. June 14th.—Heating begun, the temperature being raised slowly to 100°, and the water that was driven off collected. The temperature was maintained at 100° overnight. *June 15th—17th.*—Temperature raised to 150°; very little more water was collected. Temperature raised slowly from 150° on the morning of June 17th; at 11.45 a.m., the temperature being 250°, water made a reappearance in quantity in the distillates; at 12.45 p.m., temperature 300°, oils began to collect in the receivers, but the evolution of gases was small. The rate of production of oils increased steadily with increased temperature without a corresponding increase in the quantity of gases; between 350° and 360°, the rate of evolution of gases increases slightly, but there was no marked decomposition point until the range 370—380° was reached. *June 18th—24th.*—The sequence of events as the temperature was raised gradually to 550° was the same as with vitrain, except that a notable evolution of water occurred at 450°. As with vitrain, there was but little production of oil or tar above 480°.

The main products of the distillations, calculated as percentages, by weight, on the ash-free, dry coals, may be tabulated as follows:

<div align="center">TABLE III.</div>

	Vitrain.	Durain.
Residue (ash-free)	79·0	79·0
Water of decomposition ...	6·7	5·8
Tar and oils	5·6	8·0
Gas (by difference)	8·7	7·2

From the tar and oils there were obtained on distillation:

	Vitrain.	Durain.
Oils	3·6	4·0

The oils were composed of:

	Vitrain.	Durain.
Phenols	2·2	1·6
Neutral oils.....................	1·4	2·4

The residue remaining in the retort in each instance consisted of loose particles little different in appearance from the original materials. With durain there were slight indications of coherence of some of the particles; no coherence could be observed with vitrain. With the latter there was a shrinkage in volume amounting to about 25 per cent. of that of the original coal; with the former, the shrinkage was only about 10 per cent.

Examination of the Liquid Distillates.—Owing to the small quantities obtained, it was not possible to make a complete examination of the fractions collected at different temperatures. Up to 150°, with both vitrain and durain, the distillates consisted of water; both were neutral and colourless and free from oils and organic or mineral salts.

The distillates obtained between 150° and 300° were aqueous, with traces only of hydrocarbon oils. They fumed strongly in air, and were found to be concentrated solutions of hydrochloric acid. There was evidence of the presence of compounds of the polyphenol type in traces.

The aqueous portions separated from the distillates between 300° and 500° were also strongly acid (hydrochloric acid). On adding excess of potassium hydroxide, the vitrain distillate evolved an inflammable gas, strongly alkaline and with an odour like that of methylamine, whilst the durain distillate evolved a strongly alkaline gas, not unlike pyridine in odour. No ammonia could be detected in either distillate. Colour reactions for polyhydric phenols were again noted.

The method of examination of the tar and oils was, for both vitrain and durain, to mix together the fractions obtained at different temperatures and distil them under reduced pressure. The oils obtained were treated with solutions of sodium carbonate and potassium hydroxide to remove phenols, with hydrochloric acid to remove traces of bases, and finally with water. The phenols were liberated from their alkaline solution and distilled, as were the neutral oils. The results are best shown in parallel columns.

TABLE IV.

Vitrain.	Durain.
Below 250° (40 mm.) 64 per cent. of the tar distilled without decomposition. At 250° decomposition began. The oils that passed over at that temperature began to solidify on cooling.	Below 300° (25 mm.) 60 per cent. of the tar distilled without decomposition. Above 260° the oils coming over began to solidify on cooling. At 300° decomposition began with evolution of HCl. The oils were poured off from the solid distillate.

Examination of the oils showed:

	Vitrain.	Durain.
Soluble in dilute Na₂CO₃ solution	10 per cent.	40 per cent.
Soluble in 15 per cent. KOH solution ...	50 ,,	
Soluble in HCl	traces	traces
Neutral oils	40 per cent.	60 per cent.

TABLE IV. (*continued*).

Examination of the phenols showed:

	Vitrain.	Durain.

Vitrain.

The sodium carbonate solution contained polyphenols (o-dihydroxy).

The phenols liberated from the potassium hydroxide solution gave on distillation:

(1) 50 per cent. boiling at 200–212°.

(2) 25 per cent. boiling at 260–280°.

(3) 25 per cent. residue.

Fraction (1): $C = 76.96$; $H = 7.76$. D_{15}^{15} 1.025.

Fraction (2): $C = 78.12$; $H = 7.70$. Very viscous.

Durain.

The total phenols on distillation gave:

(1) 25 per cent. boiling at 200–220°.

(2) 25 per cent. boiling at 240–280°.

(3) 50 per cent. residue.

Fraction (1): $C = 78.49$; $H = 8.67$.

Fraction (2): $C = 80.86$; $H = 7.91$. Very viscous.

Examination of the neutral oils showed:

Vitrain.

Distilled almost completely at 160–320°.

$C = 85.86$; $H = 9.91$ $(C + H = 95.8)$.

Durain.

Distilled almost completely at 160–340°.

$C = 85.44$; $H = 10.39$ $(C + H = 95.8)$.

Charring with cold sulphuric acid left only about 10 per cent. of saturated hydrocarbons.

It will be noticed that the phenols derived from both coals fall into two well-defined groups, the first distilling at 200—220°, the second at 240—280°. The first group, in their constants and analyses, in their colour reactions with ferric chloride and other salts (aqueous and alcoholic), and in their phthalic anhydride condensations, agreed with the lower simple phenols, and were presumably cresols and xylenols. There was evidence also of the presence of some more complex phenol, or phenol ether, perhaps guaiacol. The second group gave pronounced colour reactions of the polyhydric phenols, and more particularly of the o-dihydroxybenzenes, but probably consisted mainly of condensed products. Protocatechuic acid, or a similar compound, was present in the washings from the phenols before their final distillation. This decomposes normally at about 200°, but may easily have escaped decomposition under the conditions of the distillations. Durain gave a more complex mixture of phenols than vitrain.

The distilled neutral oils from both coals were very similar, yellowish-brown oils. They did not consist exclusively of hydrocarbons, and the proportion of saturated hydrocarbons was low.

Paraffin wax was obtained in quantity from the higher boiling fractions of each tar.

The general analytic results can be summarised as follows:

TABLE V.

	Vitrain.	Clarain.	Durain.	Fusain.
Density	1·290	1·280	1·395	—
Ultimate analysis.—Per cent. on ash-free, dry coal:				
Carbon	78·5	79·1	80·8	84·7
Hydrogen	5·15	5·2	5·1	3·9
Oxygen	13·9	13·4	11·8	9·7
Nitrogen............................	1·33	1·28	1·3	1·05
Sulphur	1·12	1·02	1·0	0·65
Proximate analysis :				
Moisture, per cent.	12·6	10·2	6·5	3·9
Ash, per cent.	1·2	1·45	3·6	10·0
Volatile matter, per cent. on ash-free, dry coal	38·6	40·8	39·4	22·6
Extractions.—Per cent. on ash-free, dry coal :				
By pyridine	34·4	27·2	21·6	10·1
By alcohol	6·6	5·7	3·1	—
By chloroform	2·85	—	2·4	—
Pyridine extract soluble in chloroform, per cent.	27·0	30·0	40·0	—
Percentages of α-, β-, and γ-compounds in the coal:				
α-Compounds	65·8	72·8	78·4	—
β- ,, ...	25·0	19·0	13·0	—
γ- ,, ...	9·2	8·2	8·6	—
Action of reagents.—Per cent. on ash-free, dry coal :				
Solubility in alcoholic potassium hydroxide :				
(1) Hot	6·1	5·4	3·8	—
(2) Cold	5·7	5·2	3·6	—
Iodine absorption (permanent) :				
$N/10$-aqueous iodine, in 24 hours	22·8	23·6	17·8	4·3
Wijs's solution, in 6 hours	67·9	63·2	51·3	4·3

The general impression created by an examination of the results recorded in this table is of a gradation of properties as we pass from vitrain to durain. Fusain, as already noted, stands apart in its character from the other three ingredients of banded coal. The ultimate analyses show a steady rise in carbon and fall in oxygen content in the order (1) vitrain, (2) clarain, and (3) durain, and this order is maintained with practically every property investigated.

Thus there is a regular reduction in moisture content and increase in ash content. The marked retention of moisture by vitrain most probably results from its colloidal nature, indicated by the conchoidal fracture and the absence of any recognisable structure. The ash content may to a certain extent affect the surface lustre of the coal. Indeed, from chemical examination alone, one might be tempted to say that durain is durain because it is rich in ash; but it is clear from the work of Stopes that the decisive factor affecting the lustre is the presence or absence of plant structure. No doubt there is a direct connexion between the ash content of a coal and the presence of plant remains therein.

The results of extractions both by organic solvents and by alcoholic potassium hydroxide exhibit well the gradation in proper-. ties from vitrain to durain; they also suggest a lack of homogeneity in vitrain not evident from microscopical examination. The fact that both vitrain and durain (and, it may be assumed, clarain also) contain nearly the same proportions of γ-compounds is striking. The chief difference between the ingredients of banded coal, as revealed by the action of pyridine and chloroform, lies, therefore, in the amounts of α- and β-compounds present. If, as has been suggested, the action of pyridine is mainly a mechanical loosening of the structure of the coal conglomerate, the α- and β-compounds may actually be, as from their chemical behaviour they appear to be, essentially similar in character. From this point of view, the main difference between vitrain and durain would be a physical one, and would lie in the ease with which their (colloidal?) structures are disintegrated. The fact that the action of chloroform direct on the coals is to remove much smaller proportions of soluble matter than when an attack is first made with pyridine is in agreement with this suggestion.

Alcohol appears to dissolve a portion of the coal conglomerate unaffected by chloroform—possibly the "resins," using the word in its strictest sense. It is noteworthy that the proportions dissolved are higher than is usual with bituminous coals.

Perhaps the most striking evidence of gradation in properties of the four ingredients is afforded by the destructive distillations with examination of the gaseous products (see table III and Figs. 1 and 2). The volume–temperature curves obtained for the individual gases run nearly parallel, each to each, there being a rapid evolution of paraffins beginning at 350° and of hydrogen beginning at 400°.

The quantities of each gas (carbon dioxide excepted) evolved over equal temperature ranges are greatest with vitrain and least with fusain, clarain and durain occupying intermediate positions.

The analyses of the gases evolved from each at any given temperature interval are very similar; it is their quantity that differs. The difference between the coals—between vitrain and durain, for example—is therefore not such as exists between $\alpha + \beta$- and γ-compounds, which yield distinctive gaseous mixtures on destructive distillation, the former being rich in hydrogen and the latter rich in paraffins (Clark and Wheeler, T., 1913, **103**, 1704). The parallel volume–temperature curves show that for each of the four components of banded coal the relative production of hydrogen and paraffins is approximately the same, indicating that each contains similar proportionate amounts of the two characteristic ingredients of coal, namely, α- and β-compounds (regarded together as being similar in their behaviour on destructive distillation) and γ-compounds.

For carbon dioxide, the same order is preserved up to 400°, but is reversed at higher temperatures. With fusain, the evolution of carbon dioxide is constant for each interval of 50° between 350° and 600°.

On comparing the records of the distillations conducted on a larger scale with vitrain and durain, it will be seen that in general durain required higher temperatures to resolve it. Vitrain had a well-defined decomposition point at 350—360°, with a rapid evolution of gas and oil, whilst the decomposition point of durain was less well marked at 370—380°. Moreover, all the tar obtainable from vitrain had distilled over before a temperature of 460° was passed, whereas with durain tar was still produced at 480°.

Vitrain yielded less tar than durain, the same amount of residue, but more water of decomposition and more gas. The tar from vitrain yielded less pitch than that from durain, the quantity of oils finally obtained from the two coals being nearly the same. A difference between the distillates further appears in the character of the oils.

The high proportion of phenols in the tar oils, and the oxygenated character of the neutral oils, which contained but little saturated hydrocarbons, is noteworthy. Jones and Wheeler (T., 1914, **105**, 140) found from 12—15 per cent. of phenols in the tar oils from a Durham bituminous coal, and later (T., 1915, **107**, 1318) showed that these were produced exclusively from the "cellulosic" (α- and β-compounds) portion of the coal. The large proportion of phenols in the tar oils from the Hamstead coal used in the present research (50 per cent.) is due to the nature of the coal, which is highly oxygenated (10—13 per cent. of oxygen), a fact which also accounts for the oxygenation of the neutral oils.

It is not possible in the present state of ignorance of the chemical

composition of coal to draw precise conclusions regarding any difference in constitution that may exist between vitrain, clarain, and durain. The chemical data obtained point to the differences that might be expected to accompany the obvious difference in physical character being of degree rather than of kind. No characteristic reaction or behaviour for any one of the components of banded coal, such as might be expected were there a fundamental difference in the chemical composition of the coals, was disclosed.

The analytical results indicate for clarain a composition approximately one-third the way between vitrain and durain. It is interesting to find, therefore, that as we pass from vitrain to durain, the "reactivity" of the coal (that is to say, the extent of its susceptibility towards solvents and reagents) diminishes in the ratio vitrain : clarain : durain $= 1 : 0 \cdot 9 : 0 \cdot 7$. This relationship applies also to the results of destructive distillation (except as regards the proportions of carbon dioxide evolved).

Such a relationship can be explained on the assumption that the coals are composed of a "reactive" group of compounds, together with a relatively "inert" material. The former alone is attacked by solvents, responds to reagents, and yields the main bulk of the gases and tars on distillation. The latter is chiefly responsible for the evolution at the higher temperatures of carbon dioxide on destructive distillation, and perhaps also for the neutral oils. It is clear, also, that the "reactive" group of compounds must contain more oxygen and less carbon than the "inert."

On this assumption, vitrain, clarain, and durain are similar as regards the composition of the "reactive" material they contain, as is shown by the approximate constancy of the ratios of "reactivity," but differ in the proportions of "reactive" and "inert" constituents they contain; it is conceivable, also, that the character of the latter varies, though a consideration of the ultimate and proximate analyses of the three ingredients does not point to this being so.

Summary.

In the banded Hamstead coal investigated, the ingredients (leaving out of account fusain) show differences which grade them in the sequence vitrain, clarain, and durain. This sequence is evidenced in the fall in the moisture- and rise in ash-content; in the increase of carbon- and decrease of oxygen-content; and in the diminishing "reactivity" towards solvents, reagents, and heat treatment.

Whilst making clear interesting differences which would scarcely

have been expected from portions of coal so immediately adjacent in the same seam, the work has not revealed the presence of essentially distinct types of chemical compounds peculiar to any one of the ingredients of banded coal.

That portion of each ingredient responsible for the reactions observed appears to be of nearly constant composition. It is suggested that the difference between the ingredients lies in the proportion of "inert" or unresponsive material with which this "reactive" portion is associated. If a given weight of vitrain be assumed to contain x parts by weight of "reactive" material, the same weight of clarain would contain $0.9x$ and of durain $0.7x$ parts.

Correlation of the microscopical with the chemical and other data available respecting banded bituminous coal is reserved for a future communication.

EXPERIMENTAL.

The various operations were conducted throughout under conditions strictly comparative for the four ingredients of the banded coal.

Analyses.—For the proximate analyses, the methods recommended by the American Chemical Society were employed. The ultimate analyses were made in the usual manner, sulphur being determined by Eschka's and nitrogen by Kjeldahl's method. For the estimation of carbon and hydrogen, the combustion tube was packed with copper oxide and lead chromate. The four ingredients differed considerably in their behaviour during combustion, fusain burning with difficulty in oxygen, whilst the combustion of vitrain became uncontrollable, showers of sparks being produced. With the latter, it was found necessary to start the combustion very slowly in a stream of air, and only to use oxygen towards the end of the operation. In each instance, the result recorded is the mean of several concordant determinations.

Each sample used for combustion analysis was dried in air during one hour at 105°. Experiments at present in progress on the rates of oxidation of the coals show that such drying would have the effect of raising their oxygen content and lowering their carbon content by less than 0.1 per cent.; moreover, the amount of alteration is approximately the same for each ingredient of the banded coal.

The Action of Solvents.—The extractions with organic solvents were made in all-glass Soxhlet apparatus, the coals being enclosed in thimbles of filter paper or alundum and held in place by plugs

of glass wool. Extraction was continued until the solvent passed over colourless, and generally for as long again. The coals were stirred at intervals, and fresh charges of solvent used from time to time. The solution obtained was filtered and distilled, and the extract freed from the last traces of solvent by evaporation on a watch-glass in a vacuum or in a stream of nitrogen, being finally allowed to remain during several weeks in a vacuum over sulphuric acid.

The coals were air-dried (at 105°) for the pyridine (1 gram), dried at 105° in the absence of air for the pyridine–chloroform (10 grams), and undried for the alcohol and chloroform (5 grams) extractions. The solvents were dry and redistilled.

The Action of Reagents.—Extractions with alcoholic potassium hydroxide were made thus: (1) One gram of coal was heated with 25 c.c. of $0·7N$-potassium hydroxide in absolute alcohol at 80° during eight hours. The solution was diluted with water and filtered, and the alcohol evaporated. The "ulmin compounds" were then precipitated by concentrated hydrochloric acid, filtered from the solution, washed with distilled water, dried at 105°, and weighed. (2) For extraction in the cold, 1 gram of coal was allowed to remain during eight weeks in contact with 25 c.c. of $4N$-potassium hydroxide in 75 per cent. alcohol, with frequent shaking. The amount of extracted matter was determined as in (1).

Iodine absorptions were determined by two methods. (1) The coal, weighing $0·1$ gram, was placed in a 250 c.c. stoppered bottle with 25 c.c. of $N/10$-iodine in aqueous potassium iodide solution. The bottle was then shaken mechanically during the required time. The residual iodine was titrated with $N/10$-sodium thiosulphate solution (leaving the coal in suspension), using starch as indicator. (2) Iodine chloride in solution in glacial acetic acid was employed in place of aqueous iodine, using 10 c.c. of $N/5$-solution with $0·1$ gram of coal.

Preliminary work with different coals showed that a considerable proportion of the iodine removed from solution by the coal was evolved on keeping in contact with sodium thiosulphate solution. This evolution was not affected to an appreciable extent by the acidity of the solution, and appeared to be of iodine merely adsorbed by the coal. The adsorbed iodine was determined by adding definite volumes of sodium thiosulphate solution in excess at intervals until no further evolution could be detected, the final titration being made at the end of twenty-four hours.

Destructive Distillation. Gaseous Products.—The method of experiment and apparatus were as described by Burgess and

Wheeler (T., 1911, **99**, 639), except that 1 gram only of coal was employed without admixture with sand.

Liquid Products.—The general arrangement of apparatus and method of carrying out the distillations were similar to those employed by Jones and Wheeler (T., 1914, **105**, 140). In the place of the spherical retort used by them, a cylindrical vessel of Jena glass, 4 cm. in diameter and 14 cm. long., was employed. This form of retort allowed of a more rapid equalisation of temperature throughout the mass of the coal than the spherical form, and permitted, in consequence, more rapid distillation. The coal (about 200 grams in weight) with which the retort was completely filled was undried, and was sieved so as to pass through a 10 and remain on a 60 mesh sieve. It was held in position, when the retort was inverted during the distillation, by a plug of glass wool.

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LIII.—*The Rotation-dispersion of Butyl, Heptyl, and Octyl Tartrates.*

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ANOMALOUS rotation-dispersion is exhibited by comparatively few optically active compounds in the homogeneous state; such compounds may be conveniently classified into (1) those containing one asymmetric carbon atom, (2) those containing more than one asymmetric carbon atom, and (3) those having an absorption band in the visible part of the spectrum.

The first two of these classes and certain members of the last class exhibit a remarkable similarity in the influence which temperature and solution have on their rotation-dispersion. By examination of the circumstances in which these compounds exhibit anomalous rotation-dispersion, it is seen that in all cases *the compound becomes, or tends to become, normal in its rotation-dispersion the farther its rotation is removed from the line of zero-rotation* by the effects of temperature or dilution in solution; that is, in all cases the anomaly occurs relatively * near to the line of zero-rotation.

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* A high temperature-coefficient or dilution-coefficient is thus essential to the occurrence of the anomaly.

Much use has been made in recent years of the so-called "characteristic diagram" of Armstrong and Walker (*Proc. Roy. Soc.*, 1913, [*A*], **88**, 388) for representing the phenomena of rotation-dispersion. Such a diagram for *n*-butyl tartrate is drawn in Fig. 1A, in which are set out the specific rotations for different temperatures for the wave-lengths 4861, 5461, 5893, and 6708. It may be pointed out that in such a diagram a line is drawn at 45° to the line of zero-rotation, and on this line the rotation values for wave-length 5461 (mercury-green) are set out. Thus, for any given temperature, the position of the rotation value for λ 5461 is found on this line, and on a vertical ordinate through this point are marked the rotations at the same temperature for the other wave-lengths. After proceeding in the same way for observations made at other temperatures, the points representing the specific rotations for each wave-length are joined up by lines, which are found to be approximately straight and to intersect either in a single point or in a series of points near the line of zero-rotation.

In the above case of butyl tartrate, it will be seen that the points representing the rotations at the higher temperatures do not fall on their respective wave-length lines. This divergence is due to the maximal values for specific rotation being reached at different temperatures for different wave-lengths. The points for each wave-length thus cease to lie on a straight line when the neighbourhood of the maximum rotation is reached. Thus, in Fig. 1A especially is this the case for λ 5893 and 6708. Of course, *all* values for λ 5461 (mercury-green) lie by definition on the line drawn at 45° to the zero-line.

It is obvious that the same diagram may be used for similarly recording changes in rotatory dispersion brought about by solution and other influences, besides that of temperature.

The characteristic diagram, which thus serves to correlate the rotatory powers of many derivatives of similar constitution or of the same parent substance, has been successfully used by Pickard and Kenyon (T., 1914, **105**, 843) to predict the conditions under which β-octyl acetate would exhibit anomalous rotation-dispersion.

For most, if not all, of the substances described by Pickard and Kenyon, the characteristic diagram represents lines (for $[α]_{4359}$, $[α]_{5461}$, $[α]_{5893}$, and in some cases $[α]_{mercury-yellow}$) which do not intersect on the line of zero-rotation, but at some distance either above or below this line. If, therefore, the characteristic diagram is really indicative of the optical properties of the compounds of which the rotation values are plotted, then, obviously, all these compounds must have anomalous rotation-dispersion when the rotation assumes a value falling between zero and the value of the rotation at the

B B*

point of intersection of these lines.   Pickard and Kenyon, adopt-
ing the hypothesis of Armstrong and Walker that anomalous rota-
tion-dispersion is always due to the presence of dynamic isomerides,
ascribe the anomaly in the rotation-dispersion of some of the com-
pounds studied by them to the fact that "the esters at low tempera-
tures, and methyl-α-naphthylcarbinol at high temperatures, are, or
tend to become, really homogeneous, as the conditions of tempera-
ture favour the existence of one only of the two isomeric forms,
which have been assumed to be present" (T., 1914, **105**, 1119).
As a corollary of this, it would therefore follow that when optically
active compounds assume rotation values between zero and that of
the intersection point on the characteristic diagram, two dynamic
isomerides are present.

As already pointed out by Patterson (*Trans. Faraday Soc.*, 1914,
10, 74), however, the values of the rotation in the characteristic
diagram "do not necessarily have anything whatever to do with
the presence or absence of dynamic isomerides"; the characteristic
diagram is, in fact, a convenient method of plotting the rotation
values for different wave-lengths against the rotation value for a
particular wave-length.   It thus affords a test as to whether the
dispersion-coefficient $\Delta[a]_{\lambda_1}/\Delta[a]_{\lambda_2}$ * (Winther, *Zeitsch. physikal.
Chem.*, 1903, **45**, 373) is constant during the variation of the
rotation, which may be brought about by (1) changes in the con-
centration of the active compound in solution, (2) changes of
temperature, (3) changes of solvent, (4) changes caused by the
combination of the active compound, and (5) changes caused by
the substitution of one member of a series for another (really a
special case of No. 4).   By means of this method, in fact, a number
of isolated observations, made under varied conditions, may be
co-ordinated in one diagram.

The "rational zero," advocated by Patterson (T., 1916, **109**,
1176), when used for calculating the dispersion-coefficient gives
much more constant values than if the zero of rotation is used for
this purpose.   Moreover, the main features of the characteristic
diagram are actually summarised by the values of the rational
zeros and the rational dispersion-coefficients.

In the case of a single optically active compound, the character-
istic diagram, in part, eliminates the *accidental* condition of the
compound.   On the same diagram may be co-ordinated the rotation
values for different wave-lengths for a compound at different
temperatures, in various concentrations, in different solvents, and

* $\Delta[a]_{\lambda_1}$ and $\Delta[a]_{\lambda_2}$ are the corresponding changes produced in the
rotation for the wave-lengths λ_1 and λ_2 respectively, by varying the con-
dition of the active compound.

even in some cases in different states of combination; thus the characteristic diagram does seem to justify its name.

Compounds, the characteristic diagram of which approach the ideal represented by the lines for different wave-lengths crossing at the same point, have always normal rotation-dispersion; in such cases, the rotation value is generally little influenced by solution, change of temperature, and substitution. In such compounds, for example, menthol and its derivatives, owing to the limited range of accessible rotation values, the rotation-dispersion cannot readily be investigated under conditions in which the characteristic diagram indicates that it would be anomalous.

At the other extreme, there are compounds of which the characteristic diagram represents lines crossing in a series of points some distance from the line of zero-rotation. In these compounds, for example, tartaric acid and its esters, the rotation is generally markedly changed by the factors of temperature, solution, and substitution; in this case, it is comparatively easy to bring the rotation to such a value that the rotation-dispersion becomes anomalous. Between these two extreme types of compounds there are, of course, intermediate types. Whilst the characteristic diagram does not represent accurately the rotation-dispersion of a compound under all conditions (see Patterson, T., 1916, **109**, 1202), it nevertheless presents some advantages over previous methods of representation.

There are many facts which are difficult to explain on the hypothesis that anomalous rotation-dispersion is an indication of dynamic isomerism as postulated by Lowry and others.

Patterson (T., 1916, **109**, 1204) has shown the absurdity and incompatibility of many of the hypotheses adopted in constructing formulæ to explain dynamic isomerism.

Pickard and Kenyon (T., 1915, **107**, 42) have observed instances of complex rotation-dispersion with certain menthyl esters; if this is assumed to be due to the presence of dynamic isomerides, the existence of a *l*-menthyl ester having dextrorotatory power is postulated (since to produce anomalous dispersion, two substances of opposite rotatory power must be present; see Armstrong and Walker, *Trans. Faraday Soc.*, 1914, **10**, 88). The great improbability of this conclusion is evident from the fact that, at present, there appears to be no record of a dextrorotatory *l*-menthyl ester.

Again, compounds of similar constitution are in the one case (*a*) anomalous at high temperatures and normal at low temperatures, and (*b*) normal at high temperatures and anomalous at low temperatures (but in each case only when the temperature-rotation curve approaches zero); dimethyl acetylchloromalate is an example

B B* 2

of the first and diethyl acetylchloromalate of the second (Walden, *Zeitsch. physikal. Chem.*, 1906, **55**, 42); methyl- and hexyl-α-naphthylcarbinol are examples of the second case, whilst *aci*tetrahydronaphthylcarbinol belongs to the first category (Pickard and Kenyon, T., 1914, **105**, 1115, 2644, 2677).

A striking confirmation of the above views is found in the results obtained by Pickard and Kenyon (T., 1915, **107**, 115). The 1-naphthoate of β-hexyl-, β-heptyl-, β-octyl-, β-decyl-, and β-undecyl-carbinols are "simple"* at high temperatures and "complex" at low temperatures, the 1-naphthoate of γ-nonyl-carbinol is "simple" at low temperatures and "complex" at high temperatures, whilst the 1-naphthoate of benzylmethylcarbinol is "simple" at all temperatures. In all these cases, if the compound exhibits "complex" rotation-dispersion, this occurs as the temperature-rotation curve approaches zero; it is particularly noteworthy that, of the above compounds, the only one that is "simple" at all temperatures has a temperature-rotation curve which never approaches zero closely.

The test for "simple" and "complex" rotation-dispersion is unfortunately not definite in cases where a compound is "simple" at one temperature and "complex" at another temperature; at intermediate temperatures, it becomes impossible definitely to classify the rotation-dispersion according to these groups. In order to illustrate this distinction between "simple" and "complex" rotation-dispersion, we have drawn a diagram (Fig. 1B) for *n*-butyl tartrate in which $1/a$ is plotted against λ^2. It will be seen that whilst the low-temperature lines are curved, this curvature diminishes with rise of temperature, and at 165° the line becomes almost perfectly straight. This signifies that the rotation-dispersion of *n*-butyl tartrate is "complex" at low, but almost "simple" at high, temperatures.

It should be pointed out, again, that a substance of which the rotation-dispersion can be represented by the formula

$$[a] = K/\lambda^2 - \lambda_0^2,$$

within the limits of experimental error, that is, is "simple," may

* The terms "simple" and "complex" are here used instead of normal and anomalous because the rotation can be more easily classified into simple and complex; on plotting the values for $1/a$ against λ^2, if a straight line results then the rotation-dispersion is simple; if a curve then the rotation-dispersion is complex. It seems advisable to retain the use of both sets of terms; thus a compound is anomalous if a maximum occurs in its rotation-dispersion curve, or is normal if no maximum is present. An anomalous compound is thus always complex, whilst a normal compound is simple or complex according to its behaviour when subjected to the above-mentioned test.

not necessarily conform to this equation with more accurate determinations of the rotation; for, as Lowry points out (*Trans. Faraday Soc.*, 1914, **10**, 57), quartz, of which the rotation-dispersion, when most accurately measured, requires three such terms, that is, is "complex," can be represented *within the same limits of accuracy as are employed in the case of optically active organic compounds* by the "simple" formula. It is, in fact, highly probable that the rotation-dispersion of optically active compounds can only be represented accurately by a series of such terms. In general, however, the constants in these terms ($K_{(n)}$ and $\lambda_{0(n)}$) are sufficiently close together for one term to suffice to express accurately enough the rotation-dispersion. When a compound, by a variation of temperature or concentration in solution, becomes "complex" in its rotation-dispersion, these constants ($K_{(n)}$ and $\lambda_{\theta(n)}$) (constants for the rotation-dispersion under one condition, but varying from one condition to another) have assumed such values in the several terms that these terms can no longer be united in a single term.

In the present investigation, the rotation-dispersion of *n*-butyl, *n*-heptyl, and *n*-octyl tartrates has been observed over a wide range of temperature and for a number of wave-lengths of light.

The polarimeter used was a Schmidt and Haentsch with triple field and fitted with their dispersion attachment, the illuminant being a Nernst lamp. The prism of the dispersion apparatus was calibrated by using the spectrum lines of hydrogen, mercury, and sodium; the constants of the prism for the Hartmann formula were calculated from these measurements, and hence the reading of the scale corresponding with any desired wave-length could be found. Rotations were also measured with sodium light, and these were compared with the readings obtained with the dispersion apparatus when the scale was set at the point corresponding with the mean of the sodium lines; in all cases, these readings were equal within the limits of experimental error.

The experimental error is much greater in the violet and extreme red than in the middle part of the spectrum, owing to the difficulty in measurement and also to the reduction in luminosity.

The rotation-dispersion of methyl, ethyl, and propyl tartrates has already been investigated for a wide range of temperatures by Winther and Walden. Winther (*Zeitsch. physikal. Chem.*, 1902, **41**, 161) has recorded observations from about 20° to 100°, whilst Walden (*Ber.*, 1905, **38**, 366) measured rotations from −65° to 170°. We have investigated the rotation-dispersion of butyl tartrate from 9° to 170°, and of heptyl and octyl tartrates from their melting points up to about 170°; it was found that the com-

pounds decomposed slightly at the higher temperatures, but by again taking readings at a lower temperature, it was shown that no appreciable change in the rotation had occurred. The readings of both Winther and Walden were taken with coloured lights obtained by means of light filters; more recently, Lowry and others have determined the rotation-dispersion of methyl and ethyl

FIG. 1.
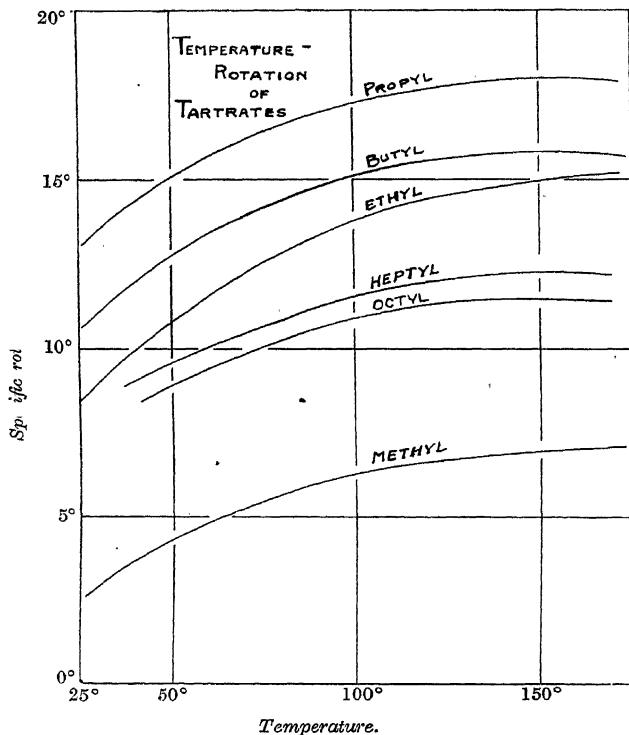
Temperature.

tartrates at two or three temperatures for different wave-lengths of light obtained from the mercury and cadmium arcs (T., 1915, **107**, 1173, 1187). The temperature-rotation curves of all these esters exhibit maxima, and for comparison, in Fig. 1, the temperature-rotation curves for sodium light for butyl, heptyl, and octyl tartrates are given, together with those obtained by Patterson (T.,

1904, **85**, 765; 1913, **103**, 173) for methyl, ethyl, and propyl tartrates.

In the following table, the temperatures at which a maximum *observed* rotation for different wave-lengths is obtained, are recorded for the several members of the series.

TABLE I.

Maxima in Observed Rotation.

	Red. 665	Yellow. 589	Green. 533	Blue. 488	Violet. 448
Methyl tartrate	160°	—	180°	—	—
Ethyl „	140	150°	155	170°	180
Propyl „	115	120	125	125	134
Butyl „	120	125	130	135	—
Heptyl „	125	130	135	140	—
Octyl „	125	130	135	140	—

Fig. 1A.

CHARACTERISTIC DIAGRAM
FOR
BUTYL TARTRATE
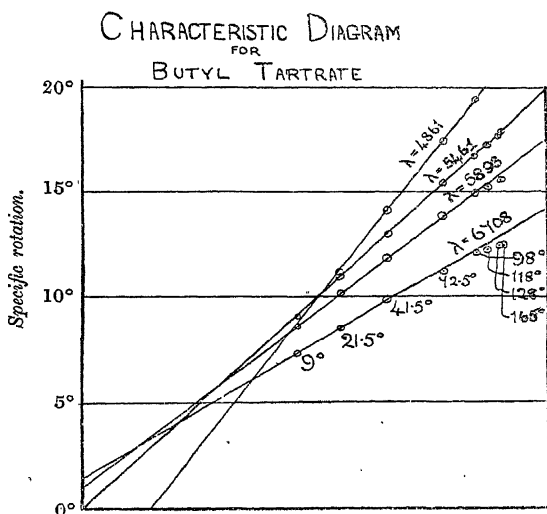
The values for the first three members of the series are taken from Walden (*loc. cit.*) and from Patterson (T., 1913, **103**, 149, 165).

In the temperature-rotation curves for butyl, heptyl, and octyl tartrates (Figs. 2, 3, and 4 respectively), the maxima in the

specific rotation for all wave-lengths lie at temperatures above 150°.

The rotation-dispersion curves for butyl, heptyl, and octyl tartrates (Figs. 5, 6, and 7 respectively) exhibit a maximum rotation at the lower temperatures only.

The following figures show the effect of ascending the series on the rotation of the tartrates.

FIG. 1B.

BUTYL TARTRATE

Inverse of rotation (1/α).

Wave-length square (λ²).
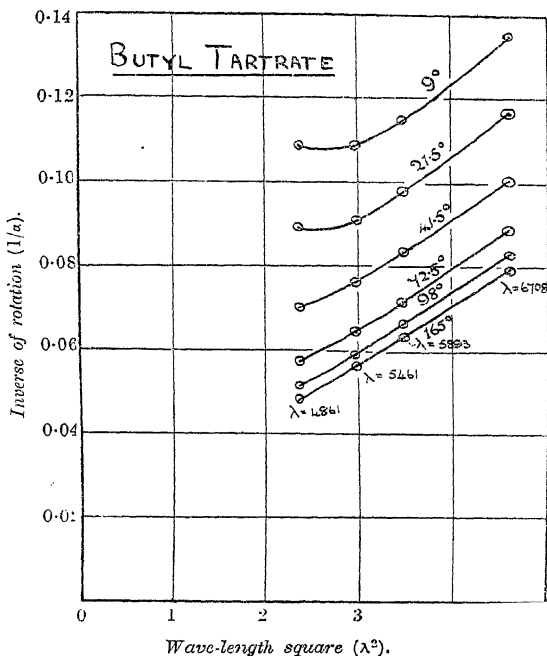
TABLE II.

	Methyl.*	Ethyl.*	Propyl.*	Butyl.	Heptyl.	Octyl.
$\alpha_D^{100°}$	7·73°	15·30°	18·25°	15·40°	10·88°	10·16°
$[\alpha]_D^{100°}$	6·18	13·70	17·20	15·00	11·44	10·84
$[M]_D^{100°}$	11·00	28·21	40·10	39·34	39·57	39·55

* Patterson (*loc. cit.*).

Thus in the observed and specific rotations there is a maximum at the propyl member of the series; but in the molecular rotation

the curve for the series increases until the propyl member is reached, after which it remains practically constant at about the

Fig. 2.
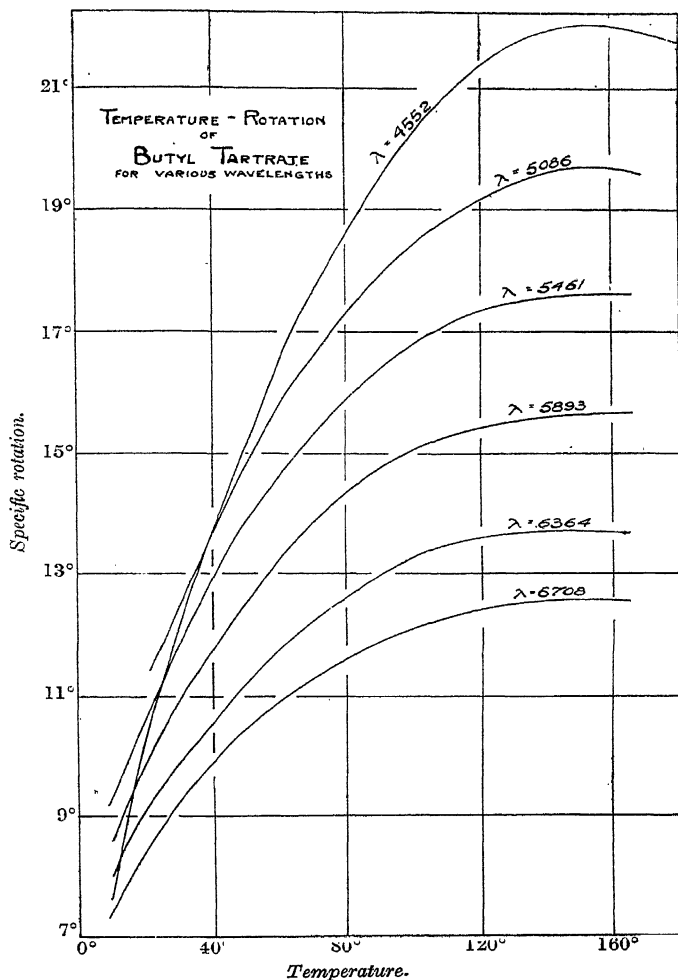
value 39·5°. It will be noticed that the maxima in the temperature-observed-rotation figures for the series (see table I) are

reached at the *lowest* temperature in the case of the propyl member.

By reference to Fig. 1, it is seen that the temperature-rotation

FIG. 3.

TEMPERATURE - ROTATION
OF
HEPTYL TARTRATE
FOR VARIOUS WAVELENGTHS·

$\lambda \cdot 4552$
$\lambda \cdot 5086$
$\lambda \cdot 5461$
$\lambda \cdot 5893$
$\lambda 6364$
$\lambda 6708$

Specific rotation.
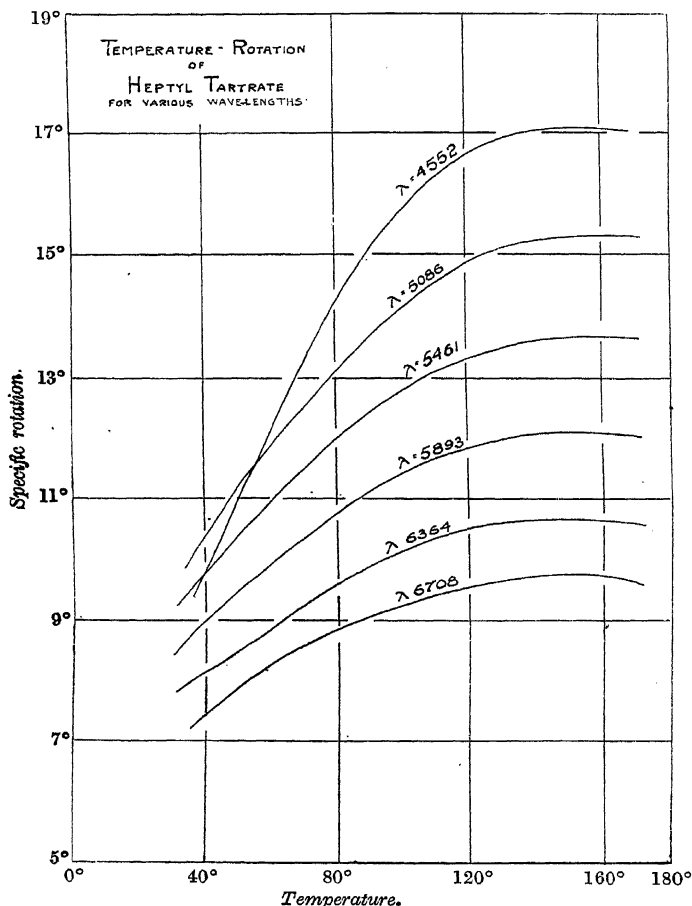
Temperature.

curves for sodium light for propyl, butyl, heptyl, and octyl tartrates are approximately parallel, therefore the maximum in the specific rotation occurs at about the same temperature for all these tartrates.

In Fig. 8, the molecular rotations for various coloured lights are shown for the several members of the series for a temperature of 100°; the molecular rotation *for all colours* remains approximately constant after the propyl member is reached.

Butyl, heptyl, and octyl tartrates are "anomalous" at low

FIG. 4.
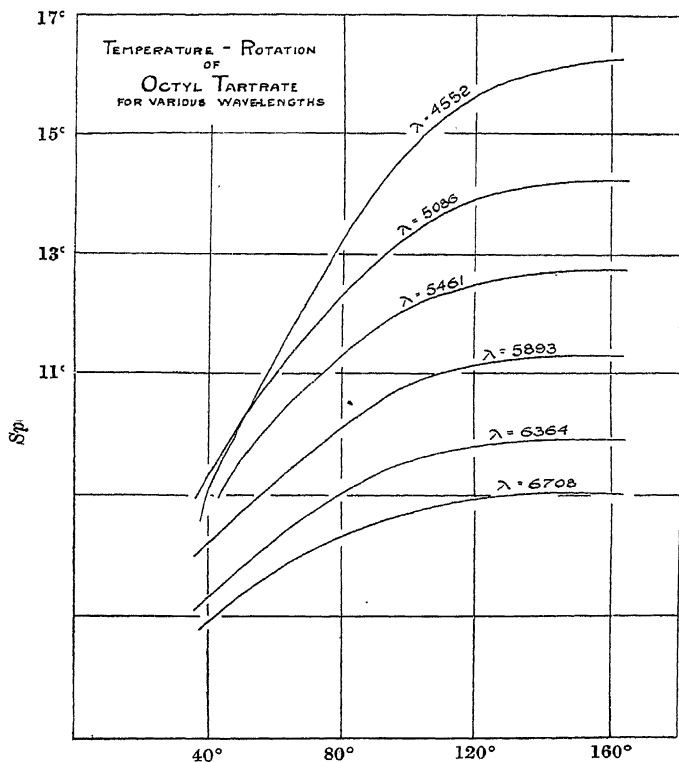
temperatures, and tend to become "normal" at high temperatures; this is readily seen by reference to Figs. 2, 3, and 4, in which the curves for the shorter wave-lengths cross the curves for the longer wave-lengths at low temperatures; the ratio, therefore, of any rotation for any wave-length to that for mercury-green

($\lambda = 5461$) varies considerably at low temperatures.   At higher temperatures, the figures in the following table show that the ratio tends to become constant.

Fig. 5.

ROTATION - DISPERSION
OF
BUTYL TARTRATE
AT VARIOUS TEMPERATURES

Wave-length.
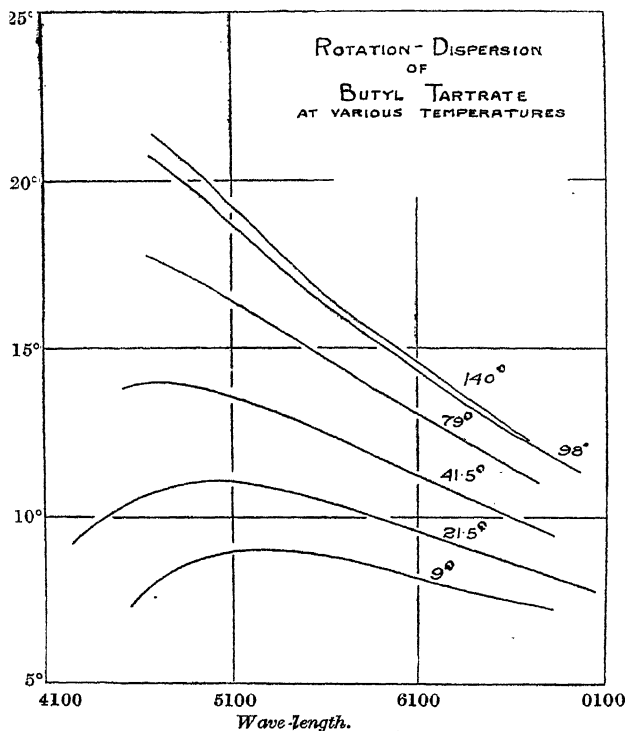
TABLE III.

		$\lambda =$	6708	5893	(Mercury Green.) 5461	5086
Butyl tartrate at 21·5°	....		0·773	0·928	1·0	1·028
,, ,, 41·5	....		0·758	0·911	1·0	1·070
,, ,, 98	....		0·723	0·892	1·0	1·098
,, ,, 128	....		0·707	0·888	1·0	1·119
,, ,, 165	....		0·709	0·888	1·0	1·113
Heptyl tartrate at 168°	....		0·707	0·886	1·0	1·116
Octyl tartrate at 165°	....		0·707	0·886	1·0	1·114

The ratios for butyl, heptyl, and octyl tartrates for the same wave-lengths are approximately equal at the higher temperatures;

whilst these ratios are rather high, they are not sufficiently high to indicate that the esters are abnormal in their rotation-dispersion. On applying the test for "simple" and "complex" rotatory dispersion (see footnote, p. 640), however, it is found that at all temperatures the rotation-dispersion is complex, but the farther the rotation is removed from the zero line by raising the tempera-

FIG. 6.
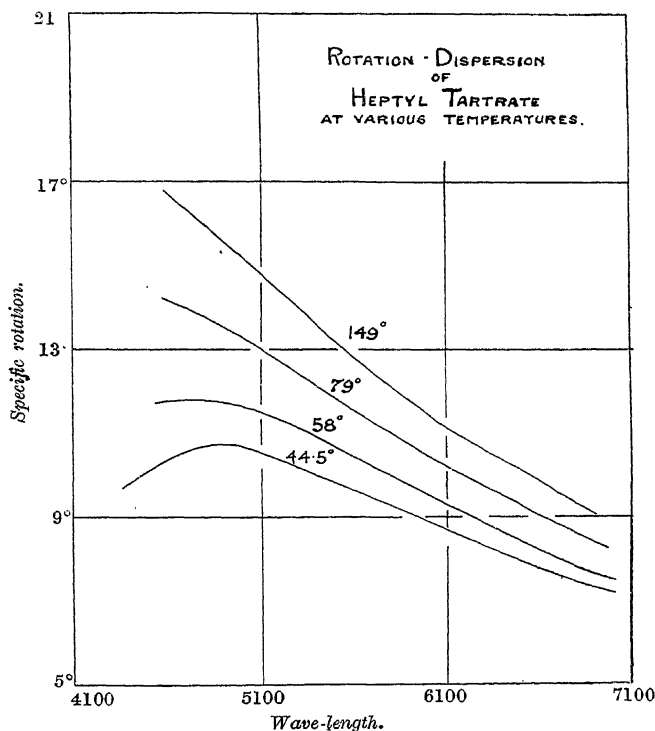
ture, the more simple (or less complex) does the rotation become; thus at high temperatures the curve $1/\alpha$ against λ^2 has only a very slight curvature, for example, see Fig. 1B.

EXPERIMENTAL.

The esters were prepared by a modification of the usual hydrochloric acid method of esterification; four molecular proportions of alcohol and one of acid were mixed and saturated with dry

hydrogen chloride while the mixture was heated on a water-bath. After leaving the mixture for a few weeks, it was again saturated with hydrogen chloride, this time in the cold; the hydrochloric acid, water, and excess of alcohol were distilled off, and the residual ester was then distilled in a partial vacuum of 12 mm. (in the case of heptyl and octyl tartrates, recrystallisation from light petroleum

FIG. 7.

ROTATION - DISPERSION
OF
OCTYL TARTRATE
AT VARIOUS TEMPERATURES
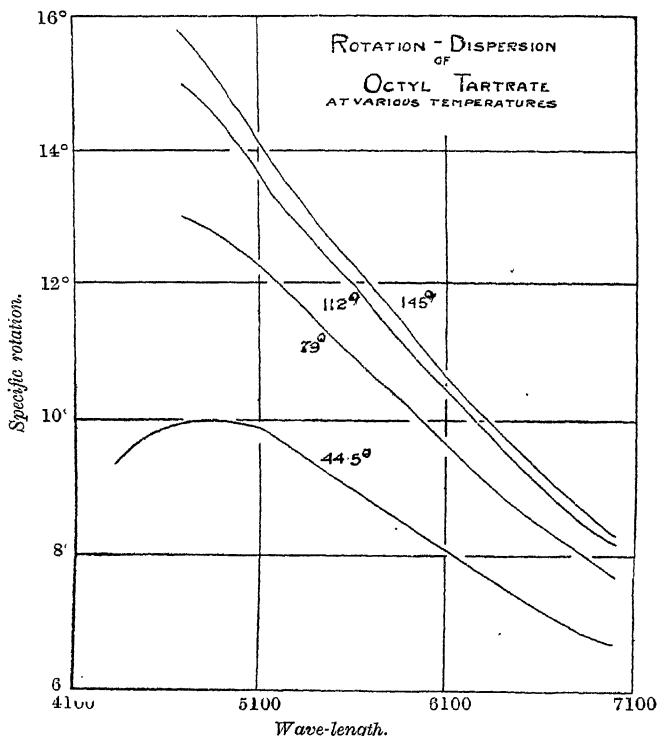
was also adopted for the purification of the residual ester). By this method of esterification, an almost theoretical yield of ester (calculated on the acid used) was obtained.

In the case of heptyl tartrate, specimens were also prepared in the following ways:

(1) The mixture of acid and alcohol was saturated with hydrogen chloride in the cold, the hydrochloric acid being removed, after

several weeks, by keeping in a desiccator; the ester crystallised out, and was recrystallised from light petroleum.

The heptyl tartrate obtained in this way had a_D^{100} 10·90°.

(2) Patterson and Dickinson's method (T., 1901, **79**, 280) was employed, commencing with ethyl tartrate. The product had a_D^{100} 10·85°.

The heptyl tartrate prepared by the method given above had a_D^{100} 10·88°, and thus no appreciable racemisation is produced by this method of esterification.

FIG. 8.
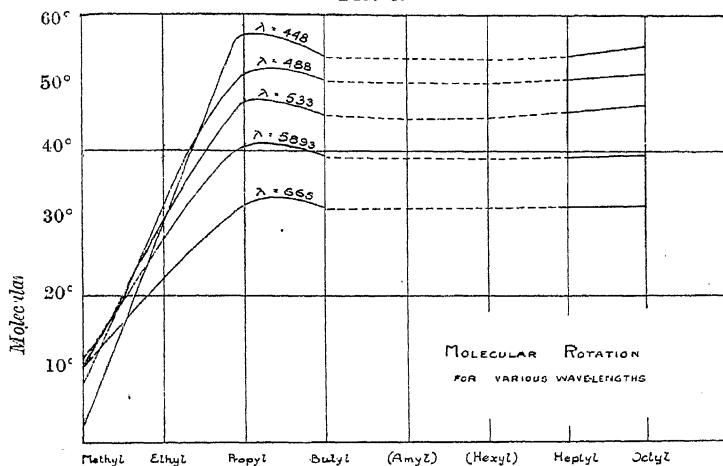
n-Butyl tartrate was prepared from butyl alcohol boiling at 116·5—117°/752 mm. (The boiling point of pure *n*-butyl alcohol is 116·5—117·2°/760 mm.) After six distillations in a vacuum of 12 mm., the butyl tartrate had $a_D^{21\cdot5}$ 22·25° ($l=2$-dcm.); this rotation is slightly less than that recorded by Freundler (*Ann. Chim. Phys.*, 1893, [vii], **3**, 446), namely, a_D^{19} 22·51° ($l=2$-dcm.). A specimen of butyl tartrate prepared from a slightly impure alcohol (b. p. 115—117°), however, we found to have a_D^{22} 24·64° ($l=2$-dcm.). Butyl tartrate melts at 22° (Freundler, *Bull. Soc. chim.*, 1894, [iii], **11**, 309, gives 21—22°) and boils at 178°/12 mm. (Freundler gives 208°/12 mm.). It exhibits a maximum in its rotation-dispersion within the wave-lengths recorded at temperatures below 70°.

Densities.

Temperature	18°	61·0°	101·2°	132·5°	169·5°
D	1·0968	1·0600	1·0246	0·9986	0·9654

Temperature 9°. Density ·044.

λ	6708	563	6147	5893	5769	5671	5570	5461	5219	48	4662
α (l=2-dcm.)	16·44	·96	18·3	19·16	19·48	19·7	19·98	20·18	20·47	19·	17·9
[α]	7·44	·68	8·3	8·67	8·82	8·9	9·04	9·13	9·26	8·	8·1
[M]	19·5	·14	21·8	22·76	23·14	23·4	23·73	23·97	24·31	23·	21·3

Temperature 25°. 1·0934

λ	692	6708	6563	5893	·64	6147	5769	5893	6025	679	5568
α	17·8	18·69	19·24	20·08	20·08	21·05	22·80	22·25	21·63	15	23·60
[α]	8·1	8·55	8·80	9·18	9·18	9·63	10·45	10·20	9·91	10 61	10·81
[M]	21·4	22·43	23·09	24·09	24·09	25·26	27·41	26·75	26·01	27 84	28·38

Temperature 45°.

λ	546	5323	5219	5154	5086	5004	4925	4861	4662	4552
α (l=2-dcm.)	24·00	24·39	24·54	24·59	24·66	24·61	24·56	24·50	24·0	23·4
[α]	11·00	·18	11·25	11·27	11·30	11·28	11·26	11·23	·0	10·7
[M]	28·86	2 33	29·51	29·57	29·65	29·59	29·53	29·46	28·8	28·2

Density ·0759

λ	5708	6563	6364	6147	6025	5893	5769	5679	5461
α (l=2-dcm.)	1·36	22·00	23·11	24·26	24·94	25·66	26·39	26·89	28·14
[α]	·93	10·22	10·74	11·27	11·59	11·92	12·27	12·50	13·08
[M]	04	26·83	28·18	29·58	30·41	31·29	32·18	32·79	34·31

λ	23	5219	5105	50	5004	4861	4785	4662	4552
α	71	29·28	29·83	30·	30·22	30·54	30·6	30·5	30·4
[α]	34	13·61	13·86	13·	14·04	14·19	14·2	14·1	14·1
M	01	35·70	36·38	36·	36·85	37·2	37·3	37·2	37·1

Temperature 72·5°. η 1·0492.

λ	6708	6563	6364	6147	6025	5893	5769
α (l 2-dm)	23·74	24·61	·93	·47	28·29	29·18	30·13
[α]	11·31	11·73	·36	·41	13·48	13·91	14·36
[M]	29·68	30·77	42	·06	35·37	36·49	37·69
				·27			

λ	5670	5568	5461	5219	5086	4861	4662
α (l 2-dm)	30·75	31·58	32·41	34·12	35·09	36·6	37·6
[α]	14·65	15·05	15·44	16·26	16·72	17·4	17·9
[M]	38·45	39·49	40·51	42·67	43·88	45·8	47·0

Temperature 98°. Density 1·0269.

λ	692	6563	6364	6147	6025	58	5769	5671
α (l 2-dm)	24·	25·76	27·15	28·74	29·70	30·	31·72	32·5
[α]	11·	12·54	13·22	13·99	14·46	14·	15·45	15·8
[M]	··	32·91	34·69	36·72	37·95	39·	40·62	41·5

λ	51	546	5086	61	4662	45i	4359
α (l 2-dm)	35	34·4·	37·80	·90	41·4	41·	41·6
[α]	16	16·75	18·40	·43	20·2	20·	20·2
[M]	··	43·90	48·29	·98	52·9	53	53·1

Temperature 118°. Density ·0099.

λ	6978	6563	6364	6147	6025	5893	5769	5679
α (l=)	23·2	25·91	27·32	29·00	29·94	1·01	32·10	32·92
α]	11·5	12·83	13·53	14·36	14·82	5·35	15·89	16·30
M]	30·1	33·66	35·49	37·68	38·90	0·29	41·70	42·77

λ	·568	5323	5219	5154	86	4861	4662	4552
α (l=)	3·97	36·29	37·14	37·79	·44	40·82	42·3	42·7
α]	16·82	17·97	18·39	18·71	·03	20·21	20·9	21·1
M]	44·13	47·14	48·25	49·10	·94	··03	54·9	55·5

Temperature 28°

$D_{e;}$ y 00

λ	6708	6563	6364	6147	6025	5893	5769
α (l=1-dcm.) ...	12·4	12·92	13·64	14·53	14·97	15·55	16·10
[α]	12·4	12·91	13·63	14·51	14·95	15·53	16·08
[M]	32·5	33·86	35·75	38·09	39·24	40·76	42·20

λ	5679	5568	5461	5219	5086	4861	4785
α (l=1-dcm.) ...	16·48	16·99	17·55	18·67	19·5	20·4	21·0
[α]	16·46	16·97	17·53	18·65	19·5	20·4	21·0
α	43·20	44·53	46·0	48·92	51·2	53·5	55·0

Temp. 40°

y 9906

λ	6708	6563	6364	6147	6025	5893	5769
α (l	24·65	25·77	27·09	28·82	29·86	1·00	32·15
[α]	12·44	13·00	13·67	14·54	15·08	5·65	16·23
[M]	32·65	34·13	35·88	38·16	39·56	·06	42·58

λ	5461	5323	5219	5154	5086	4861	4662	4652	4552
α (l	34·92	36·42	37·41	38·01	38·88	11·14	42·5	43·6	—
[α]	17·63	18·38	18·88	19·18	19·62	10·76	21·4	22·0	—
[M]	46·25	48·24	49·55	50·34	51·50	4·49	56·3	57·7	—

λ	5568
	33·97
	17·15
	14·99

[The upper portion of this page contains a large rotated (sideways) data table of optical rotation and density values for butyl, heptyl, and octyl tartrates. The rotation makes individual column alignments uncertain; legible column labels include $n.p.$, $51°.$, 98, $D_{...}$, $T_{...}ype.$, $re\ 165°.$, 969, $Den...y$, *with accompanying symbols* α, $[\alpha]$, $[M]$.*]*

n-*Heptyl tartrate*, $C_{18}H_{34}O_6$, which has not previously been described, was prepared from heptyl alcohol boiling at 175—176° (pure heptyl alcohol boils at 175·5°). It melts at 35—35·5° and boils at 228°/12 mm. and 235°/14 mm. It has α_D^{100} 21·76° ($l=2$-dcm.). Its rotation-dispersion curves exhibit maxima between the wave-lengths recorded for temperatures below 70°. It was found impossible to supercool heptyl and octyl tartrates below more than 5° of their melting points without crystallisation occurring.

Densities.

Temperature	41·0°	67·1°	105·3°	131·1°
D_4^t	0·9985	0·9776	0·9473	0·9283

Temperature 44·5°. Density 0·9952.

λ	α (l=1 dm)	[α]	[M]
6708	15·25	7·66	26·56
6563	15·76	7·92	27·44
6364	16·53	8·30	28·79
6147	17·31	8·70	30·14
6025	17·80	8·94	31·00
5893	18·26	9·17	31·79
5769	18·77	9·43	32·68
5679	19·18	9·64	33·40
5568	19·58	9·84	34·10

λ	α (l=)	[α]	[M]
5461	19·97	10·03	34·78
5323	20·43	10·27	35·58
5219	20·78	10·44	36·19
5154	21·02	10·56	36·60
5086	21·14	10·62	36·81
5004	21·3	10·70	37·1
4861	21·45	10·77	37·35
4662	21·0	10·6	36·6
4454	20·1	10·1	35·0

Temperature 58°.

λ	α	[α]	
6708	8·06	8·18	28·36
6563	8·31	8·44	29·24
6364	8·70	8·83	30·62
6147	9·15	9·29	32·20
6025	9·37	9·51	32·98
5893	9·70	9·85	34·14
5769	10·01	10·17	35·23
5679	10·23	10·39	36·01
5568	10·46	10·62	36·82

λ	α (l=1 dm)	[α]	[M]
5461	10·70	10·86	37·66
5323	10·95	11·12	38·54
5219	11·20	11·37	39·42
5154	11·33	11·50	·88
5086	11·46	11·64	40·33
5004	11·60	11·78	40·83
4861	11·70	11·88	41·18
4662	11·7	11·9	41·3
4454	11·5	11·7	40·6

Temperature 79°. Density 0·9685.

λ	α (l=2 dcm.)		
6708	17·19	8·87	30·76
6563	17·83	9·20	31·90
6364	18·69	9·65	33·44
6147	19·67	10·16	35·20
6025	20·36	10·51	36·43
5893	21·07	10·88	37·70
5769	21·74	11·23	38·90
5679	22·26	11·49	39·83
5568	22·82	11·78	40·84

λ	α		
5461	23·39	12·08	41·85
5323	24·19	12·49	43·29
5219	24·65	12·73	44·11
5154	25·16	12·99	45·02
5086	25·52	13·18	45·69
5004	25·90	13·37	46·35
4861	26·51	13·69	47·44
4662	27·3	14·1	48·85

Density 0·9520. *Temperature* 100°.

λ	α (l=2-dcm.)	[α]	[M]
6708	17·66	9·27	32·15
6563	18·27	9·59	33·26
6364	19·32	10·15	35·17
6147	20·40	10·71	37·14
6025	21·02	11·04	38·26
5893	21·76	11·43	39·61
5769	22·48	11·81	40·92
5679	23·07	12·12	42·0
5568	23·68	12·44	43·11

λ	α (l=2-dcm.)	[α]	[M]
5461	24·34	12·79	44·31
5323	25·24	13·26	45·95
5219	25·90	13·60	47·15
5154	26·35	13·84	47·97
5086	26·74	14·04	48·68
5004	27·24	14·31	49·6
4861	28·10	14·76	51·15
4662	28·9	15·2	52·7
4454	29·7	15·6	54·1

Density 0·9442. *Temperature* 110°.

λ	α (l=2-dcm.)	[α]	[M]
6708	17·92	9·49	32·89
6563	18·59	9·84	34·12
6364	19·53	10·34	35·85
6147	20·66	10·94	37·92
6025	21·34	11·30	39·17
5893	22·14	11·72	40·64
5769	22·86	12·11	41·96
5679	23·40	12·39	42·95
5568	24·10	12·76	44·24

λ	α (l=2-dcm.)	[α]	[M]
5461	24·82	13·14	45·56
5323	25·78	13·65	47·32
5219	26·74	14·16	49·08
5154	27·15	14·38	49·83
5086	27·58	14·60	50·62
5004	28·20	14·93	51·76
4861	28·77	15·24	52·8
4662	30·4	16·1	55·9
4359	31·2	16·5	57·3

Density 0·9328. *Temperature* 125°.

λ	α (l=2-dcm.)	[α]	[M]
6708	18·03	9·66	33·50
6563	18·66	10·00	34·68
6364	19·66	10·54	36·52
6147	20·82	11·16	38·68
6025	21·54	11·55	40·02
5893	22·32	11·96	41·47
5769	23·10	12·38	42·92
5679	23·72	12·71	44·07

λ	α (l=2-dcm.)	[α]	[M]
5568	24·42	13·09	45·37
5461	25·15	13·48	46·72
5219	26·98	14·46	50·12
5154	27·66	14·83	51·39
5086	28·04	15·03	52·09
5004	28·60	15·33	53·13
4861	29·44	15·78	54·69
4662	30·8	16·5	57·2

Temperature 34°.   Density 0·9258.

λ	6708	6563	6364	6147	6025	5893	5769	5679	5568
α	18·06	18·69	19·75	20·83	21·59	22·36	23·10	23·63	24·39
[α]	9·75	10·10	10·67	11·25	11·66	12·07	12·48	12·76	13·17
[M]	33·81	34·98	36·97	38·99	40·41	41·85	43·24	44·23	45·66

λ	5461	5323	5219	5154	5086	5004	4861	4662	4359
α	·12	26·16	26·90	27·49	28·00	28·69	29·60	30·7	32·1
[α]	·56	14·13	14·53	14·85	15·12	15·49	15·98	16·6	17·3
[M]	·02	48·97	50·35	51·46	52·41	53·71	55·41	57·5	60·1

Temperature 49°.   Density 0·914.

λ	6708	6563	6364	6147	...	5893	5769	5671	5558
α	8·94	9·30	9·79	10·37	...	11·10	11·52	11·7	12·18
[α]	9·78	10·17	10·71	·1·35	11·74	12·14	12·60	12·8	13·33
[M]	33·8	35·2	37·05	39·25	40·6	42·0	43·6	44·6	46·1

λ	5461	5323	5219	5154	5086	5004	4861	4662	4359
α	12·53	13·16	13·50	13·81	14·06	14·34	14·79	15·4	16·2
[α]	13·71	14·40	14·77	15·11	15·38	15·69	16·18	16·9	17·7
[M]	47·4	49·8	51·1	52·25	53·2	54·25	56·^	58·5	61·3

Temperature 68°.   Density 0·8995.

λ	6708	656	6364	6147	6025	6893	5769		5568
α	17·41	18·11	19·12	20·33	21·00	21·80	22·65	5	23·91
[α]	9·68	10·0	10·63	11·30	11·67	12·12	12·59	22	13·29
[M]	33·50	34·89	36·84	39·17	40·46	42·00	43·64	12 44	46·06

λ	5461	5323	5219	5154	5086	5004	4861	4 32	4359
α	24·62	25·53	26·41	27·03	27·49	28·19	29·15	3 ·3	31·4
[α]	13·69	14·19	14·68	15·03	15·28	15·67	16·20	1 ·8	17·4
[M]	47·43	49·19	50·88	52·08	52·96	54·31	56·16	5 4	60·5

n-*Octyl tartrate*, $C_{20}H_{38}O_6$, was prepared from octyl alcohol boiling at 194—195·5° (pure *n*-octyl alcohol boils at 195°). It melts at 41—42° and boils at 252°/16 mm. It has α_D^{100} 20·32° ($l = 2$-dcm.).

A maximum is present in the rotation—dispersion curve at 45°.

Densities.

Temperature	54·1°	73·5°	100·3°	135·1°
D_4'	0·9746	0·9601	0·9380	0·9112

Octyl Tartrate.

Temperature 45°. Density 0·9817.

568	5679	5769	5893	6025	6147
7·83	17·44	17·13	·6·70	16·27	15·81
9·08	8·88	8·73	8·51	8·29	8·05
4·02	33·28	32·69	3·87	31·05	30·17

Temperature 79°. Density 9551.

4662	4861	5004	5086	5154	5219
19·5	19·60	19·49	86	6·25	54
9·9	9·98	9·93	36	18·80	··
37·3	37·4	37·2	88	·84	
			95	36·88	

Temperature 89°. Density 9473.

5568	5679	5769	5893	6025	6147
1·10	20·54	20·08	19·44	19·27	18·69
1·05	10·75	10·51	10·18	10·17	9·86
1·39	40·29	39·39	38·13	38·11	36·96

4662	4861	5004	5086	5154	5219
24·8	24·30	23·93	23·52	23·30	22·96
13·0	12·72	12·53	12·31	12·20	12·02
48·7	47·67	46·94	16·14	45·70	45·04

5568	5769	5893	6025	6147	6364
21·67	20·58	19·95	19·27	18·60	17·24
11·44	10·86	10·53	10·17	9·32	9·02
42·86	40·70	39·46	38·11	36·96	·3·82

56	5769	5004	5086	5154	5219
21·	25·39	23·93	24·33	24·06	22·96
11·	13·40	12·53	12·84	12·70	12·53
41·	50·22	46·94	48·11	47·58	46·95

46	4861			5219	6563
26	25·39	·04		23·74	16·75
13	13·40	·74		12·53	8·84
51	50·22	·06		46·95	33·13

6563	6708
16·40	14·02
8·59	7·14
32·17	26·76

6563	5323	5461
14·44	18·65	·24
7·35	9·50	·29
27·56	35·6	8

5323	5461	6708
22·24	21·63	16·18
11·64	11·32	8·54
43·62	42·43	32·00

5323	5461
22·96	22·28
12·12	11·76
45·42	44·06

Temperature 112°. Density 9292.

λ	6708	6563	6364	6147	59..	5893	5769	5679	5568
α (l ..)	16·54	17·20	18·12	19·24	19·88	10·56	21·26	21·80	22·49
[α]	8·90	9·26	9·75	10·35	10·70	11·06	11·44	11·73	12·30
[M]	33·35	34·68	36·53	38·81	40·08	41·47	42·87	43·95	46·10

λ	5461	5323	5219	51..	5086	5004	4861	4662
α (l ..)	23·08	23·92	24·76	25·.	25·56	26·04	26·94	27·9
[α]	12·42	12·87	13·32	13·.	13·75	14·01	14·50	15·0
[M]	46·54	48·23	49·92	50·.	51·53	52·50	54·32	56·3

Temperature 32°. Density 0·9140.

λ	6708	6563	6364	6147	6025	5893	5769	5679
α (l ..)	16·53	17·17	18·11	19·21	19·86	20·59	21·30	21·82
[α]	9·04	9·39	9·91	10·51	10·87	11·26	11·65	11·93
[M]	33·88	35·20	37·12	39·38	40·71	42·20	43·66	44·72

λ	5461	5323	5219	5154	5086	4861	4662
α (l ..)	23·17	23·89	24·80	25·20	25·74	27·34	28·5
[α]	12·68	13·07	13·57	13·78	14·08	14·96	15·6
[M]	47·49	48·97	50·83	51·65	52·96	56·04	58·5

De y 0·9035

45°.

Te

65°

y 887

n p e

	6708	6563	6364	6147	6025	5893	5769	5679	5568
α	16·38	17·0	17·95	19·11	19·77	20·50	21·20	21·71	22·41
$[\alpha]$	8·06	9·4	9·93	10·58	10·94	11·34	11·73	12·01	12·40
$[M]$	33·97	35·2	37·22	39·63	40·99	51	43·96	45·02	46·47
	6708								

	5461	5323	5219	5154	5086	5893	4861	4662	
α	23·01	23·89	24·69	25·	25·66	26·17	27·24	28·5	
$[\alpha]$	12·73	13·22	13·66	13	14·20	14·48	15·07	15·8	
$[M]$	47·71	49·54	51·20	52	53·20	54·27	56·48	59·1	

	6708	6563	6364	6147	6025	5893	5769	5679	5568
α	16·05	16·70	17·65	18·70	19·39	20·10	20·82	21·39	22·09
$[\alpha]$	9·05	9·41	9·95	10·54	10·93	·33	11·74	12·06	12·45
$[M]$	33·90	35·27	37·28	39·50	40·96	46	43·98	45·18	46·66

	5461	5323	5219		5086	5893	4861	4662	
α	22·70	23·59	24·37	51	25·28	25·80	26·68	28·4	
$[\alpha]$	12·80	13·30	13·74	24·	14·25	14·54	15·04	16·0	
$[M]$	47·95	49·83	51·47	52·	53·40	54·49	56·37	60·0	

C C

LIV.—*The Tannin of the Canadian Hemlock* (Tsuga Canadensis, *Carr.*).

By RODGER JAMES MANNING and MAXIMILIAN NIERENSTEIN.

ALTHOUGH the chemistry of the pyrogallol tannins, of which gallotannin is the best known representative, has progressed during the last fifteen years, little or nothing has been published on the catechol (phlobaphen-producing) tannins, to which group nearly all the technically important vegetable tanning materials belong. We have investigated hemlock tannin, a representative of this group, in view of its colonial importance, and have accumulated observations during the three and a-half years this work has been in progress which we describe in this paper, without, however, attempting to draw any conclusions as to the probable constitution of hemlock tannin. Those who are acquainted with the literature on gallotannin (compare Dekker, " De Looistoffen," 1906; Nierenstein, " Chemie der Gerbstoffe," 1910; Dekker, " Die Gerbstoffe," 1913; Perkin and Everest, " The Natural Organic Colouring Matters," 1918) will be struck by the numerous formulæ which have been suggested for gallotannin, and the contradictory results that have been obtained. This is due to the amorphous character of gallotannin in particular and the tannins in general, and it is for this reason that we give our results on hemlock tannin without committing ourselves at this juncture to any theoretical discussion on the subject.

Böttinger's Bromo-hemlock Tannin.

Böttinger (*Ber.*, 1884, **17**, 1041) examined the action of bromine on tannin extracts, and determined the percentage of bromine contained in the precipitated bromo-compounds. On the basis of the bromo-compounds obtained from mangrove, hemlock, quebracho, mimosa, chestnut, *Terra japonica*, and spruce, he proposed formulæ for these tannins which are more or less generally accepted. Böttinger's formula for hemlock tannin is $C_{20}H_{18}O_{10}$; he deduced this from his bromo-derivative, $C_{20}H_{14}O_{10}Br_4$, from which he also prepared the acetyl derivative, $C_{20}H_9O_{10}Br_4Ac_5$. We have made a careful re-investigation of Böttinger's work on hemlock tannin, with the following results :

(1) Böttinger's bromination method does not always yield the same product, $C_{20}H_{14}O_{10}Br_4$, which requires Br = 43·60 per cent.,

but a series of compounds in which the bromine content varies from 40 to 49 per cent. The analyses of eleven preparations gave:
Br = 41·28, 47·56, 43·88, 40·12, 43·20, 47·29, 44·56, 41·74, 48·48, 41·56, and 43·26 per cent.

(2) If Böttinger's product is obtained, it can be fractionated into a number of compounds in which the bromine content varies from 40 to 48 per cent. The fractionation method employed by us consisted in dissolving the bromo-compound in acetone and fractionally precipitating by the addition of chloroform. Three such experiments were made, and the results were:

Experiment I.—Bromine content of product, 43·12 per cent.

Fractions:		II.	III.	IV.	V.
Br	=	45·63	46·82	46·96	48·09 per cent.

Experiment II.—Bromine content of product, 43·88 per cent.

Fractions:	I.	II.	III.	IV.	V.
Br	= 40·22	42·84	44·22	47·86	48·56 per cent.

Experiment III.—Bromine content of product, 43·98 per cent·

Fractions:	I.	II.	III.
Br	= 41·98	44·56	46·22 per cent.

(3) If hemlock tannin is prepared and fractionated by the method described later, and the different fractions are brominated separately, a series of bromo-compounds is obtained in which the bromine content increases as the phlobaphen content decreases.

Brominated Phlobaphens.				*Brominated Hemlock Tannin.*				
Frac-tions:	I.	II.		Frac-tions:	I.	III.	V.	
Br	= 38·59	42·33%		Br	= 43·56	46·82	47·40%	
Br	= 39·14	41·56%		Br	= —	46·77	48·09%	
Br	= 40·11	42·82%		Br	= —	46·96	48·22%	
Br	= —	—		Br	= —	—	49·56%	

Our results suggest that Böttinger's formula for hemlock tannin and bromo-hemlock tannin must be disregarded, which conclusion, probably, also applies to the other bromo-tannins mentioned.

Alkali Hydrolysis of Bromo-hemlock Tannin.

During his investigations on bromo-quebracho tannin, Nierenstein (*Collegium*, 1905, 69) obtained on hydrolysis with alcoholic potassium hydroxide (1) *iso*vanillic acid, and (2) a substance, $C_3H_7O_4Br$, to which he assigned provisionally the name monobromoquebrachilic acid. The latter crystallised from chloroform in small needles melting at 119—120°. We have extended these investi-

gations to bromo-hemlock tannin, but were only able to isolate a substance, $C_8H_7O_4Br$, which apparently is closely allied to mono-bromoquebrachilic acid, and is provisionally called *monobromo-tsuginic acid*. For comparison, the melting points of these two substances and of their derivatives are tabulated.

Monobromoquebrachilic Acid.		*Monobromotsuginic Acid.*	
Free acid ...	m. p. 119—120°	Free acid ...	m. p. 143—145°
Methyl ester	m. p. 96— 98°	Methyl ester	m. p. 108—111°
Ethyl ester...	m. p. 93— 94°	Ethyl ester	m. p. 100—102°

Nierenstein (*loc. cit.*) obtained from monobromoquebrachilic acid on further hydrolysis monobromoresorcinol, but we have failed to isolate any definite disintegration product from mono-bromotsuginic acid.

Alkali Hydrolysis.—About 10 grams of bromo-hemlock tannin containing 44·56 per cent. of bromine were heated under reflux on a water-bath with 100 c.c. of 20 per cent. alcoholic potassium hydroxide for six hours, and the solution was filtered after dilution with water. The filtrate was evaporated to dryness and extracted with acidified boiling alcohol. After several days, a crop of needles (about 0·1 gram) was obtained, which was collected and recrystallised from alcohol and benzene. Repetition of the hydrolysis gave amounts of crude monobromotsuginic acid varying from 0·7 to 1·2 per cent. of the weight of bromo-hemlock tannin.

Monobromotsuginic acid crystallises from alcohol and benzene in small, sharp needles which melt at 143—145°, carbon dioxide being evolved.

Found: $C = 38·75$; $H = 3·42$; $Br = 31·62$.   M.W. = 251.
$C_8H_7O_4Br$ requires $C = 38·87$; $H = 2·87$; $Br = 32·39$ per cent.
M.W. = 247.

The *methyl* ester, prepared by the hydrochloric acid method, crystallises from chloroform in silky needles melting at 108—111°.

Found: $C = 41·95$; $H = 3·67$.
$C_9H_9O_4Br$ requires $C = 41·38$; $H = 3·44$ per cent.

The *ethyl* ester crystallises from alcohol in needles melting at 100—102°.

Found: $C = 43·22$; $H = 4·58$.
$C_{10}H_{11}O_4Br$ requires $C = 43·63$; $H = 4·00$ per cent.

The *acetyl* derivative is prepared by digesting monobromo-tsuginic acid with acetic anhydride for several hours, the excess of acetic anhydride being removed in a vacuum. It separates from

alcohol in small, cubic crystals melting at 124—126°, carbon dioxide being evolved.

Found : $C = 41\cdot22$; $H = 3\cdot64$.
$C_{10}H_9O_5Br$ requires $C = 41\cdot52$; $H = 3\cdot12$ per cent.

Attempts to prepare carbethoxy- and benzoyl derivatives failed, as the products did not crystallise.

So far as it is possible to deduce from the above data, monobromotsuginic acid may be regarded as having the constitution $CO_2H\cdot C_7H_5OBr\cdot OH$.

Much work, however, is still required before it will be possible to decide on a definite constitution for this fission product, which in time may prove of importance to the chemistry of hemlock tannin in particular and the catechol tannins in general.

Preparation of Hemlock Tannin.

The finely sieved hemlock bark (about 8 kilos. were used each time) was extracted repeatedly with acetone. The extraction must always be carried out in the cold, on account of the ease with which hemlock tannin is oxidised to phlobaphens. The united acetone solutions were evaporated to one-third of their bulk under diminished pressure at about 55°. In this and in the succeeding operations, great care must be taken to keep the temperature as low as possible, as otherwise a considerable loss of hemlock tannin occurs through the formation of phlobaphen.

In order to precipitate the phlobaphens, the concentrated acetone solution was poured into twice its bulk of water and allowed to remain overnight. The phlobaphens, which appeared as a bulky, dark red mass, were collected, washed, and dried in a desiccator. The filtrate, which contained the hemlock tannin and always a certain amount of unprecipitated phlobaphens, was evaporated to a viscid mass in a vacuum at a temperature not exceeding 55°. This was dissolved in 570 c.c. of alcohol, and if still rich in phlobaphens gave a further precipitation if diluted with an equal amount of water. Usually, only a small portion of the alcoholic solution was tested, so as to avoid loss through oxidation. If, then, on adding water to a test portion little or no precipitation of phlobaphens took place, the whole alcoholic solution was evaporated to dryness under diminished pressure at 55°. On the other hand, if much phlobaphen was precipitated, the solution was diluted with an equal amount of water, and the preceding operations were repeated. The resultant mass (about 300 grams) was

carefully dried, and appeared then as a dark red, brittle substance, evidently still rich in phlobaphens.

The crude hemlock tannin (100 grams) was extracted with 750 c.c. of carefully dried acetone. The acetone was added in several portions and filtered before each fresh addition. The residue insoluble in acetone appeared, when carefully washed with light petroleum and dried in a vacuum at 70°, as a pale brown powder, which weighed about 5 grams. The dark red acetone solution was treated with portions of 50, 100, and 400 c.c. of chloroform, as used by Nierenstein in the purification of gallotannin (*Annalen*, 1912, **388**, 243). The first two fractions were dark and inclined to be viscid. The third fraction was pink. When washed with light petroleum and dried in a vacuum, they weighed respectively 8, 12, and 35 grams. The filtrate from fraction III was evaporated to dryness under diminished pressure at 55°, and the residue dissolved in 150 c.c. of ethyl acetate, which when poured into 200 c.c. of chloroform yielded 26 grams of a light-coloured precipitate. The filtrate was again evaporated to dryness, the residue dissolved in 100 c.c. of ethyl acetate, and fractions V and VI were precipitated by successive addition of 100 c.c. of chloroform. Fraction V (10 grams) was faintly pink, whilst fraction VI (2 grams) was creamy-white.

Found:

Fraction III.—C = 61·58, 61·86; H = 5·05, 5·29.
Fraction IV.—C = 63·52, 63·30; H = 5·31, 5·33.
Fraction V.—C = 64·09; H = 5·41.
Fraction VI.—C = 64·24, 64·06, 64·33; H = 4·88, 5·08, 5·23 per cent.

The amorphous character of the products and also the variations in the composition of the different fractions show how undesirable it is to calculate an empirical formula for hemlock tannin, as is also the case with gallotannin (compare Nierenstein, *Annalen*, 1912, **388**, 243). In addition to this, hemlock tannin also contains traces of a methoxy-compound, from which we have not succeeded in freeing it. We found that even the purest fraction (VI) contained OMe = 0·80, whilst some of the other fractions gave as much as 3·56 per cent. of methoxyl.*

* During these investigations, experiments were also made to see if some of the methoxyl in the hemlock tannin showed resistance towards hydriodic acid, and we therefore re-heated the Perkin-Zeisel apparatus on the following day after the methoxy-estimations had been carried out, as described by Herzig (*Monatsh.*, 1905, **25**, 603; 1908, **29**, 263) during his investigation of ellagic acid. We were thus able to observe an increase in the methoxy-content which, however, could be accounted for by the formation of a

Purified hemlock tannin is a pink, amorphous powder which does not melt when heated above 300°, but begins to decompose at about 260—275°. It is soluble in alcohol, acetone, ethyl acetate, or water, in which it forms deep red solutions. When hydrolysed according to Fischer and Freudenberg's method (*Ber.*, 1912, **45**, 915) for the estimation of sugar in gallotannin, it was found that hemlock tannin does not contain any kind of sugar. With iron chloride it gives a deep green coloration, especially in alcoholic solution. Hemlock tannin is precipitated by gelatin or alkaloids, and is quantitatively absorbed by caseinogen (compare Körner and Nierenstein, *Chem. Zeit.*, 1911, **36**, 31; Nierenstein, *Annalen*, 1912, **388**, 224; Spiers, *J. Agric. Sci.*, 1919, **6**, 77).

Alkali Hydrolysis of Hemlock Tannin.

(1) *Alcoholic Potassium Hydroxide.*—The only definite fission product obtained by this method was protocatechuic acid, crystallising from water in small needles melting at 191—194°, carbon dioxide being evolved. When mixed with protocatechuic acid, no depression (m. p. 193—194°) was observed.

(2) *Alcoholic Barium Hydroxide.*—We originally used aqueous barium hydroxide with some success, but later employed the methyl-alcoholic solution (compare Müller, T., 1915, **107**, 874). This hydrolysis yielded protocatechuic acid, 2:3-dihydroxybenzoic acid, and a new substance, $C_{10}H_8O_3$, which was apparently an *aldehyde.*

The hydrolysis was carried out by heating about 10 grams of hemlock tannin with an excess of methyl-alcoholic barium hydroxide for eight to ten hours under reflux. The alcohol was then removed on the water-bath, and the residue diluted with water and acidified with dilute sulphuric acid. The liquid, and also the barium sulphate precipitate, were extracted several times with ether, and the ethereal solution (solution *A*) treated with sodium hydrogen carbonate solution saturated with carbon dioxide. The aqueous part thus obtained was acidified and extracted with ether (solution *B*), and both ethereal solutions were investigated separately.

Ethereal Solution A.—The solution left, on evaporation, a tarry

precipitate of silver iodide when hydriodic acid and acetic anhydride are left for twenty-four hours and then heated (Manning and Nierenstein, *Ber.*, 1913, **46**, 3983. Critics of this note (compare G. Goldschmiedt, *Ber.*, 1914, **47**, 389; A. G. Perkin and Oesch, T., 1914, **105**, 2352) appear to have overlooked the necessity of allowing the mixture to remain for at least a day before any precipitation of silver iodide can be obtained.

mass, which became solid on rubbing and kneading with light petroleum. The dry solid was then extracted in a Soxhlet apparatus with benzene, when the greater part of the product dissolved, leaving a tarry residue in the thimble. The benzene was evaporated to dryness, and the residue (about 0·8 gram) crystallised from alcohol and benzene, from which it separated in small, silky plates melting at 125—126°. It is also soluble in alcohol or much benzene or toluene, from which solutions it crystallises in needles (m. p. 125—126°) after strong concentration of the solvents.

Found: $C = 68·45$; $H = 4·83$.   M.W. $= 160, 166$.

$C_{10}H_8O_3$ requires $C = 68·18$; $H = 4·54$ per cent.   M.W. $= 176$.

With phenylhydrazine it forms a *phenylhydrazone*, which crystallises from glacial acetic acid in dark brown needles melting and decomposing at 191°.

Found: $N = 17·91, 17·49$.

$C_{16}H_9O_2N_2$ requires $N = 17·27$ per cent.

When oxidised on the water-bath with potassium permanganate in alkaline suspension, it yields the *acid*, $C_9H_7O_2 \cdot CO_2H$, which crystallises from water in long, prismatic needles melting at 214—216°, carbon dioxide being evolved.

Found: $C = 62·42$; $H = 4·60$.

$C_{10}H_8O_4$ requires $C = 62·50$; $H = 4·20$ per cent.

The *sodium* and *potassium* salts were prepared and crystallised from water.

Found: $Na = 11·12$; $K = 20·86$.

Calculated: $Na = 10·74$; $K = 20·40$ per cent.

Diazomethane yields the *methyl* ester, which crystallises from benzene in silky needles melting at 152—153°.

Found: $C = 64·24$; $H = 4·82$.

$C_{11}H_{10}O_4$ requires $C = 64·18$; $H = 4·62$ per cent.

Ethereal Solution B.—The residue which was left on evaporation of the ether crystallised from water in small needles melting indefinitely between 145° and 168°, although the product was recrystallised several times from that solvent. The only definite colour reactions obtained were those of protocatechuic acid, and the analytical data also agreed for a dihydroxybenzoic acid. (Found: $C = 54·12$; $H = 4·22$. $C_7H_6O_4$ requires $C = 54·52$; $H = 3·94$ per cent.) Attempts were made to separate the mixture by fractional crystallisation, but no fraction of a definite melting point was obtained. The product when heated with soda-lime only gave, so far as could be ascertained, catechol (small needles from

benzene, m. p. 102—103°), from which we concluded that the mixture consisted probably of protocatechuic acid (m. p. 198—199°) and 2 : 3-dihydroxybenzoic acid (m. p. 204°) (compare Praxmarer, *Monatsh.*, 1906, **27**, 1199; also abstract of this paper, A., 1907, **92**, i, 216, where the melting point is wrongly given as 240°). The product was therefore treated in ethereal solution with diazomethane and converted into the methyl esters of veratric acid (m. p. 59—60°) and 2 : 3-dimethoxybenzoic acid (m. p. 57—58°) (compare Praxmarer, *loc. cit.*), and the mixture fractionated under diminished pressure. Sixteen grams of the methyl esters gave the following fractions, which crystallised from benzene on subsequent solidification:

Fraction I.—1·84 Grams, b. p. 124—127°/10—11 mm., m. p. 47—53°.

Fraction II.—4·26 Grams., b. p. 124—126°/10—12 mm., m. p. 52—54°.

Fraction III.—4·47 Grams, b. p. 125—127°/10—12 mm., m. p. 55—56°.

Fraction IV.—2·12 Grams, b. p. 126—129°/10—11 mm., m. p. 58—59°.

Each fraction was hydrolysed on the water-bath with alkali, and the free methoxy-acids were crystallised from dilute alcohol. These fractions melted as follows:

Fraction I.—M. p. 162—168°.

Fraction II.—M. p. 178—180°. Mixed m. p. with veratric acid, 178—180°; mixed m. p. with 2 : 3-methoxybenzoic acid, 158—164°.

Fraction III.—M. p. 176—183°. Mixed m. p. with veratric acid, 164—171°; mixed m. p. with 2 : 3-dimethoxybenzoic acid, 172—178°.

Fraction IV.—M. p. 184—186°. Mixed m. p. with veratric acid, 168—174°; mixed m. p. with 2 : 3-dimethoxybenzoic acid, m. p. 183—185°.

The melting point of veratric acid is given as 181° (compare Freund and Niederhofheim, *Ber.*, 1896, **29**, 858; Kostanecki and Tambor, *Ber.*, 1907, **39**, 4022). There is, however, no reference to 2 : 3-dimethoxybenzoic acid. This was therefore prepared by the action of diazomethane on 2 : 3-dihydroxybenzoic acid prepared according to Praxmarer's method (*loc. cit.*); the ester was subsequently hydrolysed and the methoxy-acid crystallised from dilute alcohol, from which it separated in needles melting at 187—188°, carbon dioxide being evolved. (Found: C=59·14; H=5·72. $C_9H_{10}O_4$ requires C=59·31; H=5·54 per cent.)

C C*

From the above data, it is probable that fraction II consisted mainly of veratric acid (Found: $C = 59.12$; $H = 5.78$. Calc.: $C = 59.31$; $H = 5.54$ per cent.), whereas fraction IV consisted of 2 : 3-dimethoxybenzoic acid (Found: $C = 58.92$; $H = 5.46$. Calc.: $C = 59.31$; $H = 5.54$ per cent.), from which we conclude that protocatechuic and 2 : 3-dihydroxybenzoic acids are formed during the hydrolysis of hemlock tannin.

Methylated Hemlock Tannin.

Hemlock tannin was methylated with diazomethane in ethereal suspensions, fractions IV, V, and VI only being used for the methylation. The dry tannin was suspended in ether, as used in the Grignard reaction (compare Clibbens and Nierenstein, T., 1915, **107**, 1491), and an excess of diazomethane allowed to act on it for about twelve hours. In the case of fraction IV there was always a residue, after methylation, insoluble in ether [similar observations were made by Herzig (*Monatsh.*, 1912, **33**, 843), and Fischer and Freudenberg (*Ber.*, 1912, **45**, 2723), during the methylation of gallotannin with diazomethane]. Fraction V also left a small residue, but fraction VI on methylation dissolved completely in ether.

The ethereal solution was filtered and the ether removed under diminished pressure. The residue was purified by dissolving in a little alcohol and pouring into water. It frequently happened that the methylated product did not separate out readily, in which case the liquid was shaken vigorously to coagulate the precipitate and allowed to remain for a time. The precipitate was then collected, carefully washed, and dried in a desiccator.

Methylated hemlock tannin obtained in this way after several precipitations was a white, amorphous product with a more or less distinctly yellow tint; it was readily soluble in alcohol, ether, acetone, benzene, carbon tetrachloride, or *s*-tetrachloroethane, but insoluble in light petroleum. The product had no definite melting point; it sintered at 74—79° and melted at 134—141°.

Found: $C = 65.69$, 65.25, 64.82, 65.12; $H = 5.58$, 5.46, 5.82, 5.27; $OMe = 26.48$, 25.65, 25.84 per cent. M.W. (in chloroform) $= 620$, 561, 552, 574.

The methoxy-estimations were carried out in a Zeisel-Perkin apparatus, acetic anhydride being added. If the latter was replaced by phenol (compare Weishut, *Monatsh.*, 1913, **33**, 1165), the same result was obtained ($OMe = 25.76$ per cent.). In view of the experiences of W. Richter (*Diss.*, Erlangen, 1902, 44), who found that eutannin is more fully methylated with diazomethane

in an acetone solution than in an ethereal one, we also used the former as a solvent, without, however, increasing the methoxy-content. (Found: OMe $= 25 \cdot 89$ per cent.). For similar reasons, we also used methyl alcohol as a solvent (compare Geake and Nierenstein, *Biochem. J.*, 1914, **8**, 292), the result being the same (Found: OMe $= 25 \cdot 43$ per cent.).

Methylated hemlock tannin was found. to be optically active: $[\alpha]_{D}^{17}$ $-41°$ (in chloroform), $-24 \cdot 7°$ (in s-tetrachloroethane), $50 \cdot 1°$ (in alcohol), and $-16 \cdot 9°$ (in acetone).

Alkali Hydrolysis of Methylated Hemlock Tannin.

Methylated hemlock tannin (about 5—10 grams) was hydrolysed by boiling with a 10 per cent. solution of alcoholic potassium hydr-oxide for about three hours. The alcohol was then evaporated, and the residue extracted with boiling water and filtered from any incompletely hydrolysed or tarry substance. On acidifying with dilute sulphuric acid, the filtrate gave a bulky precipitate (pre-cipitate A), which was collected, washed, and dried in a desiccator. The filtrate was extracted with ether several times, and the ethereal extract treated with a 5 per cent. solution of sodium hydrogen carbonate saturated with carbon dioxide. Nothing was found to remain in the ether. The sodium hydrogen carbonate solution was acidified with dilute sulphuric acid and extracted with ether. On evaporation of the ether, a residue was obtained which was crystallised several times from water with the addition of animal charcoal, when small crystals were obtained melting at 208°. They proved to be vanillic acid, and gave no depression of the melting point when mixed with vanillic acid. (Found: $C = 57 \cdot 02$; $H = 5 \cdot 08$. Calc.: $C = 57 \cdot 11$; $H = 4 \cdot 81$ per cent.)

Precipitate A.—The product was purified by dissolving several times in alcohol and precipitating with water.

Found: $C = 67 \cdot 14$, $66 \cdot 83$; $H = 6 \cdot 49$, $6 \cdot 22$; OMe $= 28 \cdot 18$ per cent.

When oxidised with potassium permanganate in alkaline solu-tion, hemipinic acid was produced. The following method of oxidation gave the best results. 1·5 Grams of the substance were heated on a water-bath for six to eight hours with 75 c.c. of $2N$-potassium hydroxide and 3 grams of potassium permanganate dissolved in about 50 c.c. of water, which were added in two por-tions. The solution was acidified, filtered, and extracted with ether. The residue left on evaporation crystallised from water in small needles, which melted when slowly heated at 170—173° (compare Nierenstein, *Annalen*, 1913, **396**, 198; Pschorr and

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Samuleanu, *Ber.*, 1899, **32**, 3411), which melting point was not depressed when mixed with hemipinic acid prepared from opianic acid. (Found: $C = 53\cdot33$; $H = 5\cdot09$. Calc.: $C = 53\cdot07$; $H = 4\cdot47$ per cent.)

Mild hydrolysis of precipitate *A* furnished opianic acid, which was obtained on warming 2 grams of the substance with 20 c.c. of $2N$-alcoholic potassium hydroxide for several hours on the water-bath under reflux at a temperature not higher than 60°. The alcohol was evaporated, the residue acidified, and extracted with ether. The ethereal extract was shaken with sodium hydrogen carbonate solution saturated with carbon dioxide, and the aqueous part, after acidification with dilute sulphuric acid, extracted with ether. The carefully dried residue which was left on evaporation of the ether deposited, from benzene, thin, prismatic needles melting at 147—149°. When mixed with opianic acid, no depression of the melting point was observed. (Found: $C = 56\cdot82$, $56\cdot78$; $H = 5\cdot12$, $4\cdot94$. Calc.: $C = 57\cdot11$; $H = 4\cdot81$ per cent.) A small amount was converted into the oxime, crystallising in small needles melting at 81°, which is in the vicinity of the melting point 82—83°, as found by W. H. Perkin, jun. (T., 1890, **57**, 1071). There was not enough material for a combustion.

The fact that the methylated hemlock tannin yields opianic acid (I) suggests the possible existence of noropianic acid (II) in hemlock tannin, which probably explains the formation of hemipinic acid (III) and veratric acid (IV) from methylated hemlock tannin and protocatechuic acid (V) and 2 : 3-dihydroxybenzoic acid (VI) from hemlock tannin:

(I.)

(III.)

(IV.)

(II.)
(Not isolated.)

(Not isolated.)

(V.)

(VI.)
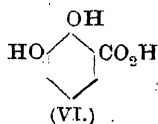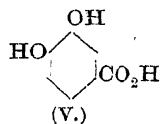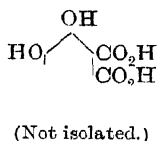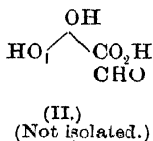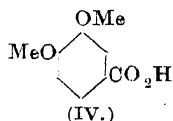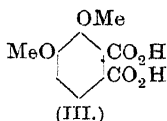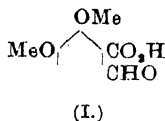
In conclusion, we wish to take this opportunity of expressing our thanks to the Research Fund Committee of the Chemical Society, and to the Colston Society of the University of Bristol, for grants towards this investigation.   We also wish to thank Messrs. Davis and Sons, Tanners, Kingston, Canada, for a generous supply of hemlock bark.

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LV.—*The Formation of Diazoamino-compounds from β-Naphthylamine.*

By GEORGE MARSHALL NORMAN.

DURING the preparation of some diazoamino-compounds involving the action of diazotised β-naphthylamine on amines of the benzene series, it was noticed that, in the case of *o*-toluidine, the product was a tarry substance which, on keeping, became a dark red solid and consisted of *o*-tolueneazo-β-naphthylamine (Norman, T., 1912, **101**, 1914).

A search has been made for other cases of this result, and as both *m*- and *p*-toluidine gave diazoamino-compounds, *o*-substituted amines have been selected for the purpose.   However, a substituent in the *o*-position, even a methyl radicle, is not the only condition necessary, for, although *m*-4-xylidine gave *m*-xylene-4-azo-β-naphthylamine, *p*-xylidine gave a diazoamino-compound, a result also obtained with *o*-chloroaniline, 3-bromo-*p*-toluidine, and 5-bromo-*o*-toluidine.   Under the same conditions, diazotised β-naphthylamine does not appreciably react with 3-nitro-*p*-toluidine or 5-nitro-*o*-toluidine, even on keeping for several hours.   The same difficulty was encountered in the case of *s*-trichloroaniline.

The diazoamino-compounds obtained pass quite readily into the isomeric aminoazo-compounds on heating with the contained benzene base and its hydrochloride.   This can be explained by the occurrence of an intramolecular change or by a preliminary decomposition into a diazonium salt and β-naphthylamine, with subsequent recombination to form the azo-compound, and this is supported by the formation of *p*-tolueneazo-β-naphthylamine on heating diazoamino-*p*-toluene with *p*-toluidine hydrochloride and β-naphthylamine in molecular proportions and excess of *p*-toluidine.

The experiments of Meldola and Streatfeild (T., 1887, **51**, 434) showed that the action of aqueous acids is to decompose mixed diazoamino-compounds into four products, the bases and the corresponding diazonium salts in molecular proportions, but under the conditions of the present experiments the only aminoazo-compound produced is derived from the diazotised benzenoid base and β-naphthylamine in practically quantitative yield. The decomposition into four products evidently does not occur, or one would expect to find β-naphthaleneazo-β-naphthylamine among the products, unless, indeed, β-naphthalenediazonium chloride in the presence of the benzene base is converted into a substituted benzenediazonium chloride.

When the diazoamino-compounds are heated with β-naphthol, either β-naphthylamine or the benzene base is eliminated, and the resulting hydroxyazo-compound is not a mixture in the cases examined. Thus, the diazoamino-compound obtained from 5-bromo-o-toluidine gave 5-bromo-o-tolueneazo-β-naphthol and eliminated β-naphthylamine, but the compounds from o-chloroaniline, 3-bromo-p-toluidine, and p-xylidine gave β-naphthaleneazo-β-naphthol and eliminated the benzenoid base. Probably this can be best explained by the formation of an unstable intermediate compound, which undergoes decomposition with the elimination of one of the bases present, the mode of decomposition depending on the nature and position of the substituent radicles.

Experimental.

m-Xylene-4-azo-β-naphthylamine, $C_6H_3(CH_3)_2 \cdot N_2 \cdot C_{10}H_6 \cdot NH_2$.

This compound crystallises from methylated spirit in orange-red plates melting at 126°:

    0·1345 gave 18 c.c. N_2 (moist) at 16° and 750 mm.   N = 15·4.
             $C_{18}H_{17}N_3$ requires N = 15·27 per cent.

The *acetyl* derivative crystallises from ethyl acetate in small, orange-red needles melting at 142°:

    0·1235 gave 13·9 c.c. N_2 (moist) at 15° and 752 mm.   N = 13·1.
           $C_{20}H_{19}ON_3$ requires N = 13·25 per cent.

The *benzoyl* derivative crystallises from ethyl acetate in bright red needles melting at 145°:

    0·1142 gave 11·2 c.c. N_2 (moist) at 17° and 756 mm.   N = 11·3.
           $C_{25}H_{21}ON_3$ requires N = 11·08 per cent.

Action of β-Naphthalenediazonium Chloride on m-4-*Xylidine.*

On the addition of sodium acetate to the cold solution, a brown solid separated which became tarry, and, on keeping, solidified to a red solid, which was identified as *m*-xylene-4-azo-β-naphthylamine.

Reduction of m-*Xylene-4-azo-β-naphthylamine.*

In order to establish beyond doubt the constitution of this compound, it was reduced with zinc dust in acetic acid solution. Acetic anhydride was then added, and the subsequent addition of a little water caused the separation of a solid, which was identified as diacetyl-1:2-naphthylenediamine, whilst from the mother liquor aceto-*m*-4-xylidide was obtained.

Action of Nitrous Acid on m-*Xylene-4-azo-β-naphthylamine.*

Meldola and East's method (T., 1888, **53**, 465) gave a tarry solid, which was boiled with alcoholic potassium hydroxide. The product was identified as *m*-xylene-4-azo-β-naphthol (m. p. 166°).

o-*Chlorobenzeneazo-β-naphthylamine*, $C_6H_4Cl\cdot N_2\cdot C_{10}H_6\cdot NH_2$.

This compound crystallises from benzene in red needles melting at 151°:

0·1520 gave 19·5 c.c. N_2 (moist) at 16° and 748 mm.   N = 14·71.
$C_{16}H_{12}N_3Cl$ requires N = 14·93 per cent.

The *acetyl* derivative crystallises from ethyl acetate in orange-red, silky needles melting at 153°:

0·1324 gave 0·5940 AgCl.   Cl = 11·1.
$C_{18}H_{14}ON_3Cl$ requires Cl = 10·97 per cent.

The *benzoyl* derivative crystallises from glacial acetic acid in orange needles melting at 167°:

0·1841 gave 0·6955 AgCl.   Cl = 9·35.
$C_{23}H_{16}ON_3Cl$ requires Cl = 9·2 per cent.

β-*Naphthalenediazoamino-o-chlorobenzene*, $C_6H_4Cl\cdot N_3H\cdot C_{10}H_7$.

This compound crystallises from toluene in pale brown, minute needles melting at 100°. When heated with *o*-chloroaniline and its hydrochloride at 60°, it changes readily into the isomeric amino-azo-compound, and when heated with β-naphthol it gives β-naphthaleneazo-β-naphthol and *o*-chloroaniline:

0·1231 gave 15·9 c.c. N_2 (moist) at 17° and 750 mm.   N = 14·8.
$C_{16}H_{12}N_3Cl$ requires N = 14·93 per cent.

3-*Bromo*-p-*tolueneazo*-β-*naphthylamine*, $C_6H_3MeBr \cdot N_2 \cdot C_{10}H_6 \cdot NH_2$.

This compound crystallises from methylated spirit in glistening, dark red plates melting at 172°:

0·1461 gave 16·0 c.c. N_2 (moist) at 18° and 752 mm.   N = 12·48.
$C_{17}H_{14}N_3Br$ requires N = 12·35 per cent.

The *acetyl* derivative crystallises from glacial acetic acid in small, yellow needles melting at 168°:

0·1324 gave 0·6459 AgBr.   Br = 20·76.
$C_{19}H_{16}ON_3Br$ requires Br = 20·94 per cent.

The *benzoyl* derivative crystallises from ethyl acetate· in orange-red needles melting at 186°:

0·1448 gave 0·6090 AgBr.   Br = 17·89.
$C_{24}H_{18}ON_3Br$ requires Br = 18·02 per cent.

4-β-*Naphthalenediazoamino*-3-*bromotoluene*,
$C_6H_3MeBr \cdot N_3H \cdot C_{10}H_7$.

This compound crystallises from methylated spirit in pale brown prisms melting at 104°. On heating with 3-bromo-*p*-toluidine and its hydrochloride at 60°, it passes readily into the isomeric amino-azo-compound, and when heated with β-naphthol eliminates 3-bromo-*p*-toluidine and gives 3-bromo-*p*-tolueneazo-β-naphthol, which crystallises from benzene in red needles melting at 169°:

0·23 gave 24 c.c. N_2 (moist) at 14° and 752 mm.   N = 12·14.
$C_{17}H_{14}N_3Br$ requires N = 12·35 per cent.

5-*Bromo*-o-*tolueneazo*-β-*naphthylamine*,
$C_6H_3MeBr \cdot N_2 \cdot C_{10}H_6 \cdot NH_2$.

This compound crystallises from methylated spirit in small, red plates melting at 152°:

0·1542 gave 16·6 c.c. N_2 (moist) at 15° and 754 mm.   N = 12·52.
$C_{17}H_{14}N_3Br$ requires N = 12·35 per cent.

The *acetyl* derivative crystallises from ethyl acetate in orange-red, feathery needles melting at 189°:

0·1643 gave 0·8115 AgBr.   Br = 21·02.
$C_{19}H_{16}ON_3Br$ requires Br = 20·94 per cent.

The *benzoyl* derivative crystallises from ethyl acetate in pale orange, feathery needles melting at 179°:

0·1862 gave 0·7859 AgBr.   Br = 17·96.

$C_{24}H_{18}ON_3Br$ requires Br = 18·02 per cent.

2-β-*Naphthalenediazoamino*-5-*bromotoluene,* $C_6H_3MeBr \cdot N_3H \cdot C_{10}H_7$.

This compound crystallises from toluene in small, red needles melting at 113°.   When heated with 5-bromo-*o*-toluidine and its hydrochloride at 65°, it passes into the isomeric aminoazo-compound, and when heated with β-naphthol it eliminates β-naphthylamine and yields 5-bromo-*o*-tolueneazo-β-naphthol, which crystallises from benzene in red plates melting at 174°:

0·1459 gave 16 c.c. N_2 (moist) at 19° and 749 mm.   N = 12·42.

$C_{17}H_{14}N_3Br$ requires N = 12·35 per cent.

p-*Xyleneazo*-β-*naphthylamine,* $C_6H_3Me_2 \cdot N_2 \cdot C_{10}H_6 \cdot NH_2$.

This compound crystallises from methylated spirit in brilliant orange-red needles melting at 119°:

0·1421 gave 18·6 c.c. N_2 (moist) at 17° and 754 mm.   N = 15·07.

$C_{18}H_{17}N_3$ requires N = 15·27 per cent.

The *acetyl* derivative crystallises from ethyl acetate in dark red needles melting at 167°:

0·1239 gave 14·2 c.c. N_2 (moist) at 15° and 750 mm.   N = 13·24.

$C_{20}H_{19}ON_3$ requires N = 13·25 per cent.

The *benzoyl* derivative crystallises from ethyl acetate in orange-red, feathery needles melting at 148°:

0·1761 gave 16·6 c.c. N_2 (moist) at 15° and 750 mm.   N = 10·9.

$C_{25}H_{21}ON_3$ requires N = 11·08 per cent.

2-β-*Naphthalenediazoamino*-p-*xylene,* $C_6H_3Me_2 \cdot N_3H \cdot C_{10}H_7$.

This compound crystallises from benzene in brownish-red crystals melting somewhat indefinitely at 120°.   On heating with *p*-xylidine and its hydrochloride, a small quantity of a yellow solid melting at 124°, and containing 11·7 per cent. of nitrogen, was obtained, but it was not further identified.   On heating with β-naphthol, it gives β-naphthaleneazo-β-naphthol and *p*-xylidine:

0·1213 gave 15·9 c.c. N_2 (moist) at 17° and 754 mm.   N = 15·09.

$C_{18}H_{17}N_3$ requires N = 15·27 per cent.

3-*Nitro*-p-*tolueneazo-β-naphthylamine,*
$NO_2 \cdot C_6H_3Me \cdot N_2 \cdot C_{10}H_6 \cdot NH_2$.

This compound crystallises from toluene in dark bronze needles melting at 224° :

0·1133 gave 18 c.c. N_2 (moist) at 18° and 753 mm.   N = 18·18.
$C_{17}H_{14}O_2N_4$ requires N = 18·3 per cent.

The *acetyl* derivative crystallises from ethyl acetate or toluene in small, red needles melting at 200° :

0·1441 gave 20·2 c.c. N_2 (moist) at 19° and 753 mm.   N = 15·95.
$C_{19}H_{16}O_3N_4$ requires N = 16·09 per cent.

The *benzoyl* derivative crystallises from ethyl acetate in red needles melting at 158° :

0·1137 gave 13·7 c.c. N_2 (moist) at 16° and 750 mm.   N = 13·86.
$C_{24}H_{18}O_3N_4$ requires N = 13·66 per cent.

5-*Nitro*-o-*tolueneazo-β-naphthylamine,*
$NO_2 \cdot C_6H_3Me \cdot N_2 \cdot C_{10}H_6 \cdot NH_2$.

This compound crystallises from toluene in dark bronze needles melting at 210° :

0·1239 gave 19·1 c.c. N_2 (moist) at 16° and 758 mm.   N = 17·93.
$C_{17}H_{14}O_2N_4$ requires N = 18·3 per cent.

The *acetyl* derivative crystallises from toluene in red needles melting at 240° :

0·1361 gave 19·2 c.c. N_2 (moist) at 17° and 754 mm.   N = 16·24.
$C_{19}H_{16}O_3N_4$ requires N = 16·09 per cent.

The *benzoyl* derivative crystallises from toluene in red needles melting at 197° :

0·1356 gave 16 c.c. N_2 (moist) at 16° and 760 mm.   N = 13·76.
$C_{24}H_{18}O_3N_4$ requires N = 13·66 per cent.

s-*Trichlorobenzeneazo-β-naphthylamine,* $C_6H_2Cl_3 \cdot N_2 \cdot C_{10}H_6 \cdot NH_2$.

This compound crystallises from benzene in red needles melting at 157° :

0·2135 gave 0·2618 AgCl.   Cl = 30·26.
$C_{16}H_{10}N_3Cl_3$ requires Cl = 30·38 per cent.

The *acetyl* derivative crystallises from ethyl acetate in reddish-yellow needles melting at 169° :

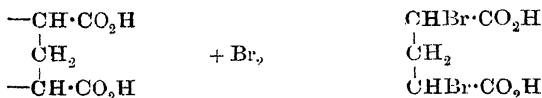0·2341 gave 0·2556 AgCl.   Cl = 27·01.
$C_{18}H_{12}ON_3Cl_3$ requires Cl = 27·13 per cent.

Action of p-*Toluidine and its Hydrochloride on Diazoamino-*p-*toluene in the Presence of* β-*Naphthylamine.*

Molecular quantities of diazoamino-*p*-toluene, *p*-toluidine hydrochloride, and β-naphthylamine were dissolved in *p*-toluidine and heated for twelve hours at 50°. On treatment with hydrochloric acid, a residue was obtained which was crystallised from methylated spirit, and melted at 112°. It was identified as *p*-tolueneazo-β-naphthylamine.

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LVI.—*The Chemistry of the Glutaconic Acids. Part XI. The Occurrence of* 1 : 3-*Addition to the Normal Form.*

By JOCELYN FIELD THORPE.

IN Part IX of this series (T., 1913, **103**, 1579) it was shown that the *cis*-labile ester of β-methylglutaconic acid, which can be readily formed by the action of alcoholic sodium ethoxide on ethyl *iso*-dehydracetate,

(1) $O{<}^{CMe\vdots C(CO_2Et)}_{CO\text{------}CH}{>}CMe$ + EtOH

$$CO_2Et \cdot CH_2 \cdot CMe\vdots CH \cdot CO_2Et + Me \cdot CO_2Et$$

condenses with the sodium compound of ethyl cyanoacetate, giving a 60 per cent. yield of a condensation product in accordance with the equation

(2) $CO_2Et \cdot CH\vdots CMe \cdot CH_2 \cdot CO_2Et$ $CO_2Et \cdot CH_2 \cdot \underset{|}{C}Me \cdot CH_2 \cdot CO_2Et$
  $+ CH_2(CN) \cdot CO_2Et$ $\overset{|}{C}H(CN) \cdot CO_2Et$

whereas the normal ester, $CO_2Et \cdot \overset{\bullet}{C}H \cdot CHMe \cdot \overset{\bullet}{C}H \cdot CO_2Et$, which can be prepared from the normal acid by etherification, yields no condensation product under the same experimental conditions.

Several other esters of normal acids of the series were subjected to the same reaction, and the failure in each case to obtain a condensation product was regarded as evidence that substances possessing the normal structure which, in accordance with the

views put forward in this series, have constitutions best represented by the general formula $CO_2R\cdot\overset{.}{C}R\cdot CHR\cdot\overset{.}{C}R\cdot CO_2R$ (R = H or alkyl), do not form additive products when treated with the usual additive reagents.

The evidence is, however, negative, and during the whole course of these researches on the glutaconic acids, frequent attempts have been made to obtain direct evidence of the structure of the normal forms by inducing them to form additive products in the 1 : 3-positions. If, for example, bromine could be made to unite with the terminal carbon atoms of the normal system, thus :

$$\begin{array}{lll} -CH\cdot CO_2H & & CHBr\cdot CO_2H \\ \overset{|}{C}H_2 & + Br_2 & \overset{|}{C}H_2 \\ -\overset{|}{C}H\cdot CO_2H & & \overset{|}{C}HBr\cdot CO_2H \end{array}$$

and if the isomeric compound produced from the labile modification were found to be formed in accordance with the scheme :

$$\begin{array}{lll} CH\cdot CO_2H & & CHBr\cdot CO_2H \\ \overset{||}{C}H & + Br_2 & \overset{|}{C}HBr \\ \overset{|}{C}H_2\cdot CO_2H & & \overset{|}{C}H_2\cdot CO_2H \end{array}$$
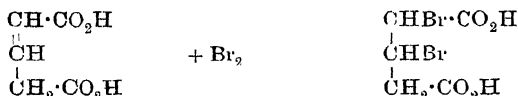
no reasonable doubt would then remain that the formulæ for the glutaconic acids suggested in this series must be a close approximation to the truth.

Unfortunately, the evidence obtained in this way is far from satisfactory. The stable normal acids of the type of β-methyl-glutaconic acid (the *cis*-acid of Feist, *Annalen*, 1906, **345**, 64, and of Fichter and Schwab, *Annalen*, 1907, **348**, 254, melting at 149°) do not react with the halogen to give any definite additive products, although the *cis*-labile acid (the *trans*-acid of Feist and Fichter, melting at 115—116°) readily forms $\alpha\beta$-dibromo-β-methyl-glutaric acid, $CO_2H\cdot CHBr\cdot CMeBr\cdot CH_2\cdot CO_2H$ (m. p. 145°), when treated with bromine in direct sunlight (Fichter and Schwab, *loc. cit.*).

On the other hand, those acids, of which glutaconic acid itself is the best example, the labile forms of which are so unstable as to be incapable of isolation, yet readily pass, either through hydroxy-anhydride formation or through the formation of the sodium derivative of the esters, into derivatives of the labile forms (T.,

$$CO_2H\cdot\overset{.}{C}H\cdot CH_2\cdot\overset{.}{C}H\cdot CO_2H$$

Glutaconic acid.

$$CH{<}^{CH:C(OH)}_{CH-\!-\!-\!CO}{>}O$$

Hydroxy-anhydride.

$$CO_2Et\cdot CH{:}CH\cdot CH{:}C(ONa)\cdot OEt$$
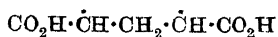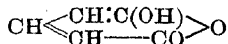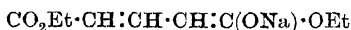
Sodium derivative of ester.

1912, **101**, 863; 1913, **103**, 1757), react with bromine in a curious
manner. For example, glutaconic acid readily absorbs the correct
amount of bromine, but no one appears to have been able to isolate
any definite product from the reaction mixture. Kiliani (*Ber.*,
1885, **18**, 2517) first studied the action of bromine on this acid.
He noticed the rapid absorption of the halogen, but, without
attempting to isolate the additive product, treated the crude reac-
tion mixture with calcium carbonate and obtained a 10 per cent.
yield of $\alpha\beta$-dihydroxyglutaric acid,

$$CO_2H \cdot CH(OH) \cdot CH(OH) \cdot CH_2 \cdot CO_2H,$$

a yield which was subsequently increased to 14 per cent (*Ber.*,
1905, **38**, 3625). Ultimately, Feist (*Ber.*, 1911, **44**, 137) was able
to obtain an 80—85 per cent. yield of the dibromo-ester,

$$CO_2Et \cdot CHBr \cdot CMeBr \cdot CH_2 \cdot CO_2Et,$$

by brominating ethyl glutaconate in sunlight.

It is evident, therefore, that the normal acids of this series do
not react with bromine in the way one would expect an $\alpha\beta$-un-
saturated acid to react, and that they only form additive products
under conditions which favour the transformation of the normal
into the labile modifications. The labile acids, on the other hand,
are easily converted into $\alpha\beta$-dibromo-additive products in accord-
ance with the properties of the structures assigned to them.

Direct evidence respecting the structure of the normal form
can, however, be obtained from a study of the condensation pro-
ducts formed from the normal and labile esters of β-methyl-
glutaconic acid with the sodium compound of ethyl cyanoacetate,
for it is now found that whereas the *cis*-labile ester reacts in accord-
ance with equation (2) and gives a yield, which has now been
increased to 80 per cent., of the 1 : 2-additive product, the normal
ester can, under special conditions described in the experimental
portion, be made to yield a small quantity (approximately 6 per
cent.) of a condensation product which, when hydrolysed, is con-
verted into γ-methylbutane-$\alpha\beta\delta$-tricarboxylic acid, in accordance
with the scheme:

$$
\begin{array}{ll}
-CH \cdot CO_2Et & \\
\quad | & \\
\ \ CHMe & + CH_2(CN) \cdot CO_2Et \\
\quad | & \\
-CH \cdot CO_2Et & \\
\end{array}
$$

$$
\begin{array}{ll}
CH_2 \cdot CO_2Et & \qquad CH_2 \cdot CO_2H \\
\quad | & \qquad\quad | \\
CHMe & \qquad CHMe \\
\quad | & \qquad\quad | \\
CH \cdot CO_2Et & \qquad CH \cdot CO_2H \\
\quad | & \qquad\quad | \\
CH(CN) \cdot CO_2Et & \qquad CH_2 \cdot CO_2H \\
\end{array}
$$
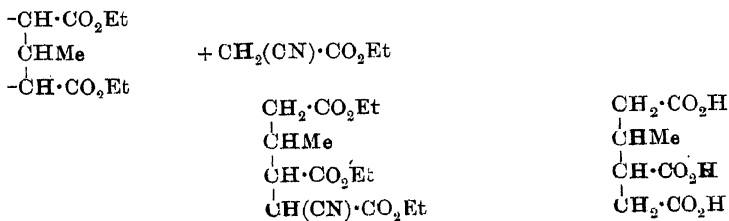
an acid which was found by direct comparison to be identical with that prepared by Hope and Perkin (T., 1911, **99**, 762) by the interaction of ethyl bromoacetate and the condensation product of ethyl sodiocyanoacetate with ethyl crotonate.

There can be no question, therefore, that in this reaction addition has been effected in the 1 : 3-positions, and although the yield is small, the formation of a condensation product having the above composition is direct evidence of the structure of the normal form.

A similar condensation tried with ethyl glutaconate failed to bring about addition in the 1 : 3-positions, and the product (about 5 per cent. yield) was found to have the structure assigned to it in the previous paper (T., 1913, **103**, 1580). It had therefore been formed in accordance with the scheme :

$$
\begin{array}{lll}
CH \cdot CO_2Et & & CO_2Et \cdot CH(CN) \cdot CH \cdot CO_2Et \\
CH & + CH_2(CN) \cdot CO_2Et & CH_2 \\
CH_2 \cdot CO_2Et & & CH_2 \cdot CO_2Et
\end{array}
$$
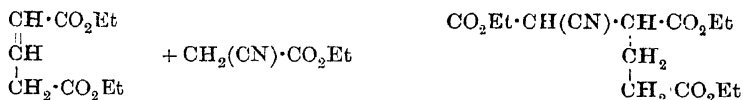
and it is evident that a small quantity of the normal ester is converted into the labile ester under the experimental conditions used. It is of interest to record at this stage a tendency that has been detected for the *cis*-labile ester to pass into the normal ester when kept. Hitherto, the *cis*-ester has been regarded as a comparatively stable substance. It distils without change, and can be hydrolysed to the corresponding *cis*-acid without conversion into the normal isomeride.

The following facts show, however, that, under certain conditions, the labile ester passes slowly into its normal form. About the middle of 1914, some 600 grams of the *cis*-labile ester had been accumulated for use in the preparation of the "enclosed" ring compound, an account of which is about to be published. It had all been prepared within the previous month, and some of it had already been used in condensation with the sodium compound of ethyl cyanoacetate, and found to give the usual yield of the condensation product. War then broke out, and the ester remaining over was laid aside until January of the present year, that is, for approximately four and a-half years. It happened that the larger quantity of the ester (about 450 grams) was placed in a deep yellow glass bottle, whereas the remaining amount (about 130 grams) was kept in a white glass bottle. Both bottles were placed side by side in a shallow cupboard with glass doors facing a strong north light. In January, 1919, the ester in the white glass bottle was noticed to have become deep brown, and when condensed with the sodium compound of ethyl cyanoacetate was found to give only 20 per

cent. of the usual condensation product. It was therefore distilled and hydrolysed, when the mixture of acids formed was found to consist of 75 per cent. of the normal acid melting at 149° and 25 per cent. of the labile acid melting at 115—116°. The ester in the yellow bottle, on the other hand, was found to have altered little in colour and to give the usual yield when condensed with ethyl sodiocyanoacetate. After distillation and hydrolysis, it was found to yield the *cis*-acid melting at 115—116° in an almost pure form, a small quantity, about 5 per cent. only, of the *trans*-acid being isolated. In order to check these results, a further quantity of the cis-labile ester was prepared from ethyl *iso*dehydracetate and hydrolysed, when the product was found to be the pure *cis*-acid.

It is evident, therefore, that exposure to light for a considerable period of time leads to the partial conversion of the *cis*-labile form into the normal modification.

<center>EXPERIMENTAL.</center>

Condensation of Normal Ethyl β-Methylglutaconate with the Sodium Compound of Ethyl Cyanoacetate.

In the earlier attempt which was made to effect this condensation (T., 1913, **103**, 1580), molecular quantities of the ingredients were used, and the mixture was heated on the water-bath for twenty-four hours. As no condensation product could be isolated under these conditions, they were altered in the present instance so as to ensure that a large excess of ethyl cyanoacetate was present throughout the reaction. Forty-two grams of the normal ester, prepared by the etherification of the normal acid, were added to an alcoholic suspension of the sodium compound of ethyl cyanoacetate prepared from 94 grams of the ester and 9·7 grams of sodium dissolved in 110 grams of alcohol, and the mixture was heated for thirty-six hours on the water-bath. Water was then added, and the acidified liquid extracted with ether. Sodium carbonate solution failed to extract any appreciable quantity of acid ester from the ethereal solution, and the latter was therefore dried and freed from ether. The residual oil was then carefully fractionated under diminished pressure, when, besides the two fractions of lower boiling point, consisting of ethyl cyanoacetate and unchanged ethyl β-methylglutaconate, a small fraction (about 4 grams) of high boiling point was isolated.

Ethyl α-cyano-γ-methylbutane-αβδ-tricarboxylate,

$$CH_2(CO_2Et) \cdot CHMe \cdot CH(CO_2Et) \cdot CH(CN) \cdot CO_2Et,$$

is a colourless, moderately viscid liquid which boils at $212°/$ 22 mm.:

0·1932 gave 0·4081 CO_2 and 0·1293 H_2O.   C$= 57·66$; H$= 7·41$.
$C_{15}H_{25}O_6N$ requires C $= 57·5$; H $= 7·4$ per cent.

γ-Methylbutane-$\alpha\beta\delta$-tricarboxylic Acid,
$CO_2H \cdot CH_2 \cdot CH(CO_2H) \cdot CHMe \cdot CH_2 \cdot CO_2H.$
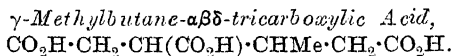
Hope and Perkin found it necessary, in order to obtain this acid in a crystalline condition, to hydrolyse their cyano-triethyl ester to the tribasic acid, to etherify this, and, after fractionation, to isolate the potassium salt by the aid of methyl-alcoholic potassium hydroxide. Apparently there is no need to use this method in order to obtain the crystalline acid from the isomeric cyano-triethyl ester described above, because the hydrolysis proceeded rapidly and smoothly through the agency of "50 per cent." aqueous sulphuric acid. Twelve grams of the cyano-triethyl ester were dissolved in an equal volume of concentrated sulphuric acid, care being taken to keep the mixture cool, and allowed to remain at the ordinary temperature for two hours. Water was then added until the solution became slightly turbid, when it was boiled under a reflux condenser for five hours, the alcohol formed during hydrolysis being removed from time to time by detaching the condenser tube from the flask. After the cooled product had been saturated with ammonium sulphate, it was extracted with ether, and the syrupy acid, which rapidly solidified, obtained by evaporating the dried ethereal solution. The crude acid was then purified by treatment with concentrated hydrochloric acid, filtering, and recrystallising from this solvent. It melted sharply at 154° (Hope and Perkin give 153—154°) (Found: C $= 46·95$; H $= 6·13$. $C_8H_{12}O_6$ requires C $= 47·1$; H $= 5·9$ per cent.).

The acid was found to crystallise in nodular masses, as described by Hope and Perkin, and mixtures of it with Hope and Perkin's acid were found to have the same melting point (154°) as either constituent. It also gave a potassium salt insoluble in methyl-alcoholic potassium hydroxide. Unfortunately, the amount of acid available was insufficient for the purpose of preparing crystalline derivatives, because the anhydro-acid is apparently one of those intractable substances which are very difficult to obtain in a crystalline condition, similar properties being possessed by the aniline and toluidine derivatives of the anhydro-acid. All attempts to prepare these substances in a crystalline condition were

unsuccessful, and it is possible that the same difficulty was encountered by Hope and Perkin, since it will be noticed that no derivatives of this acid are described by them.

The evidence of the mixed melting point is, however, usually accepted as sufficient proof of identity. In the present instance, this is, of course, strengthened by the fact that the only other acid of this formula which could be produced in the reaction, namely, $\beta\beta$-dimethylpropanetricarboxylic acid, $CMe(CH_2 \cdot CO_2H)_3$ (T., 1913, **103**, 1583), melts at 172° and readily gives a crystalline anhydro-acid, which can be converted into a crystalline anil-anilide and trianilide.

The Transformation of cis-Labile Ethyl β-Methylglutaconate into the Normal Form.

There is little to add to the general description of this change given in the introductory portion. The labile ester contained in the white glass bottle, which had previously given the usual yield of the condensation product with the sodium compound of ethyl cyanoacetate, was found at the end of four and a-half years to give a yield of only 20 per cent. under the same experimental conditions. It was therefore distilled, and was found to have the same boiling point as the original ester. When hydrolysed, it was found, however, that a mixture of acids was obtained, from which an insoluble, crystalline barium salt could be isolated in large quantities when the neutral ammonium salts of the mixed acids were treated with barium chloride solution and boiled. This was collected and converted into the acid, which was found to melt at 149° (Found: C = 49·89; H = 5·68. $C_6H_8O_4$ requires C = 50·0; H = 5·6 per cent.).

This acid, which was evidently, therefore, the normal acid, constituted approximately 75 per cent. of the mixture. The labile acid melting at 115—116° was isolated in the usual manner from the mother liquors of the barium salt precipitation.

The ester which had been kept in the deep yellow bottle, and had altered little in appearance, was found on conversion into the acids to yield only a small quantity of an insoluble barium salt, from which the acid melting at 149° was isolated. The amount constituted about 5 per cent. of the mixed acids obtained, the remainder being the cis-labile acid melting at 115—116°, which was isolated from the mother liquors. The original ester was also found to give approximately the normal yield of con-

densation product with the sodium derivative of ethyl cyanoacetate.

The change was further proved by preparing some fresh *cis*-labile ester from ethyl *iso*dehydracetate, when the product was found to yield the pure labile acid on hydrolysis.

THE IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON.   [*Received, June 3rd*, 1919.]

LVII.—*The Formation and Reactions of Imino-compounds. Part XIX. The Chemistry of the Cyanoacetamide and Guareschi Condensations.*

By GEORGE ARMAND ROBERT KON and JOCELYN FIELD THORPE.

FROM the experiments described in Part XV (T., 1911, **99**, 422) and Part XVIII (T., 1913, **103**, 1586) of this series, it can be concluded that the condensation of cyanoacetamide with ketones in the presence of piperidine yields, to an extent of approximately 95 per cent., products which have the groups attached to the terminal carbon atoms arranged in the *trans*-positions to one another, and that approximately 5 per cent. only of the condensation product has the *cis*-configuration. The proportions vary slightly with the nature of the ketone used and with the temperature at which the condensation is carried out, but is generally of the above order when the reactions are effected at the ordinary temperature.

The following considerations support this conclusion:

(1) The chief product is obtained as a base (I) soluble in dilute mineral acid, which is quickly hydrolysed by the acid to the imide (II) in accordance with the scheme:

$$
\begin{array}{ccc}
\mathrm{NH_2\cdot CO\cdot CH_2\cdot CN} & & \mathrm{NH_2\cdot CO\cdot CH\cdot C\!:\!NH} \\
\mathrm{R_2CO} & \longrightarrow & \mathrm{R_2C\quad NH} \quad \text{or} \\
\mathrm{CN\cdot CH_2\cdot CO\cdot NH_2} & & \mathrm{CN\cdot CH\cdot CO} \\
& & \text{(I.)}
\end{array}
$$

$$
\begin{array}{ccc}
\mathrm{NH_2\cdot CO\cdot CH\cdot C\cdot NH_2} & & \mathrm{NH_2\cdot CO\cdot CH\cdot CO} \\
\mathrm{R_2C\quad N} & \longleftarrow & \mathrm{R_2C\quad NH} \\
\mathrm{CN\cdot CH\cdot CO} & & \mathrm{CN\cdot CH\cdot CO} \\
\text{(I.)} & & \text{(II.)}
\end{array}
$$
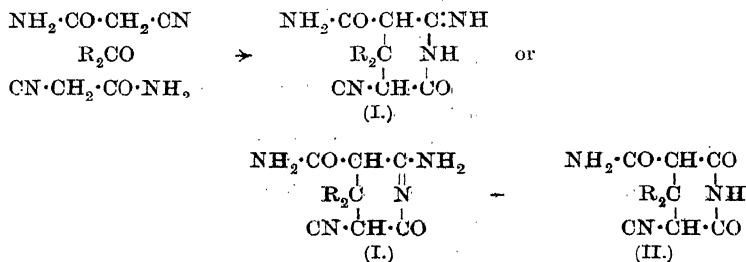
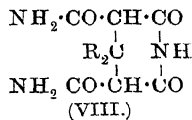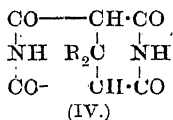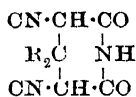The *trans*-configuration is further proved by the formation of the di-imino-di-imide (III), thus:

$$NH_2 \cdot CO \cdot CH \cdot C\!:\!NH$$
$$R_2\overset{|}{C} \quad \overset{|}{C}O$$
$$CN \cdot CH \cdot NH$$

$$CO\text{-} \quad \text{---}CH \cdot C\!:\!NH$$
$$\overset{|}{N}H \quad R_2\overset{|}{C} \quad \overset{|}{N}H$$
$$\overset{|}{C}(\!:\!NH) \cdot \overset{|}{C}H \cdot \overset{|}{C}O$$
(III.)

$$CO\text{---}\text{---}CH \cdot CO$$
$$\overset{|}{N}H \quad R_2\overset{|}{C} \quad \overset{|}{N}H$$
$$\overset{|}{C}O\text{---}\text{---}\overset{|}{C}H \cdot \overset{|}{C}O$$
(IV.)

$$CH_2 \cdot CO_2H$$
$$\overset{|}{C}R_2$$
$$\overset{|}{C}H_2 \cdot CO_2H$$
(V.)
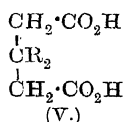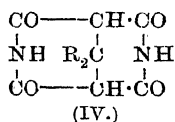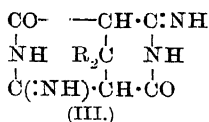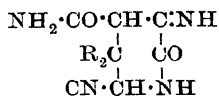
and the general structure of the whole series is shown by the production of the acid (V) from each of these compounds on complete hydrolysis.

(2) A small quantity of condensation product is also obtained which is soluble in alkali, and is evidently present in the condensation mixture as an ammonium salt (VI), since it yields the imide (VII) on treatment with mineral acids:

$$CN \cdot CH_2 \cdot CO \cdot NH_2$$
$$R_2CO$$
$$CN \cdot CH_2 \cdot CO \cdot NH_2$$

$$CN \cdot CH \cdot C(OH) \cdot NH_2$$
$$R_2\overset{|}{C} \quad \overset{|}{N}H$$
$$CN \cdot \overset{|}{C}H \cdot \overset{|}{C}O$$

$$CN \cdot CH \cdot C(ONH_4)$$
$$R_2\overset{|}{C} \quad \overset{||}{N}$$
$$CN \cdot \overset{|}{C}H \cdot \overset{|}{C}O$$
(VI.)

$$CN \cdot CH \cdot CO$$
$$R_2\overset{|}{C} \quad \overset{|}{N}H$$
$$CN \cdot \overset{|}{C}H \cdot \overset{|}{C}O$$
(VII.)
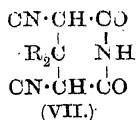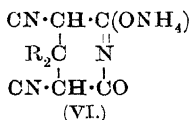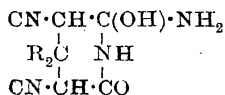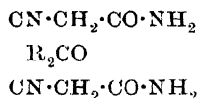
The *cis*-configuration of this substance follows from the production, with sulphuric acid, of a di-imide identical with (IV) or the

$$CN \cdot CH \cdot CO$$
$$R_2\overset{|}{C} \quad \overset{|}{N}H$$
$$CN \cdot \overset{|}{C}H \cdot \overset{|}{C}O$$

$$CO\text{---}\text{---}CH \cdot CO$$
$$\overset{|}{N}H \quad R_2\overset{|}{C} \quad \overset{|}{N}H$$
$$\overset{|}{C}O\text{-} \quad \overset{|}{C}H \cdot \overset{|}{C}O$$
(IV.)

$$NH_2 \cdot CO \cdot CH \cdot CO$$
$$R_2\overset{|}{C} \quad \overset{|}{N}H$$
$$NH_2 \, CO \cdot \overset{|}{C}H \cdot \overset{|}{C}O$$
(VIII.)

corresponding diamide (VIII), and the general structure from the fact that it yields the acid (V) on complete hydrolysis.

On the other hand, it is certain that when substances of these types are prepared by the action of alcoholic ammonia on a mixture of the ketone and ethyl cyanoacetate (Guareschi's method), there appears to be no tendency for the condensation product to assume the *trans*-structure, and the compounds prepared in this way have the *cis*-configuration, being, in fact, identical with the

substances of types (VI) and (VII) above. Guareschi's reactions are usually carried out at 40°, and if the cyanoacetamide condensations are effected at a similar temperature, the quantity of the *cis*-product is increased, but the fact that no trace of a *trans*-condensation product can be isolated under Guareschi's conditions shows that direction into *cis* or *trans* is dependent on the reaction and is not appreciably affected by the temperature.

It is evident that the cyanoacetamide condensation can also yield three other products, namely, the initial condensation product (IX) and the open-chain compounds (X) and (XI), and that the isolation of these substances must depend (1) on the

$$R_2C:C(CN)\cdot CO\cdot NH_2 \qquad \begin{array}{c} CN\cdot CH\cdot CO\cdot NH_2 \\ R_2C \\ CN\cdot CH\cdot CO\cdot NH_2 \end{array} \qquad \begin{array}{c} NH_2\cdot CO\cdot CH\cdot CN \\ R_2C \\ CN\cdot CH\cdot CO\cdot NH_2 \end{array}$$

(IX.)   (X.)   (XI.)
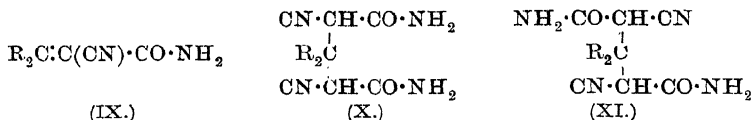
tendency for the double compound to form, and (2) on the tendency which exists for the six-membered ring to be produced. As regards (X) and (XI), we have not been able to isolate any trace of them in ketone condensations, although, as will be shown in a subsequent paper, they are the chief products when certain aldehydes are used in place of ketones. The formation of (IX) has been noticed in one case, which is described in this paper, and its production and reactions clearly show the general mechanism of these condensations. It was found, for example, that when *cyclo*pentanone is condensed with cyanoacetamide under conditions which usually yield the cyclic imino-compound (type I), the product is the unsaturated amide (XII).

$$\begin{array}{c} CH_2\cdot CH_2 \\ CH_2\cdot CH_2 \end{array}\!\!>\!\!C:C(CN)\cdot CO\cdot NH_2 \qquad \begin{array}{c} CH_2{-}CH \\ CH_2\cdot CH_2 \end{array}\!\!>\!\!C\cdot C(CN)\cdot CO_2H$$

(XII.)   (XIII.)

$$\begin{array}{c} C(:NH){-\!\!-\!\!-}CH\cdot CO \\ NH \ \ C_4H_8{:}C \ \ NH \\ CO{-\!\!-\!\!-\!\!-}CH\cdot C(:NH) \end{array}$$

(XIV.)
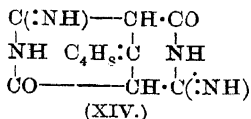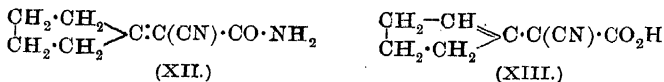
It is true that this amide yields, on treatment with nitrous acid, α-cyano-Δ¹-*cyclo*pentenacetic acid (XIII), identical with the compound obtained by Harding and Haworth (T., 1910, **97**, 486), but the fact that it readily condenses with more cyanoacetamide to form the di-imino-compound (XIV) is, we think, proof that it must have the formula (XII). Its precipitation in the present instance is due entirely to its insolubility in the aqueous medium

used, because, if sufficient alcohol is employed, the reaction pursues a normal course with the direct production of the di-imino-derivative (XIV). The production of this intermediate product is, however, of interest, since it is probable that in all cases of this kind the initial condensation leads to the formation of the unsaturated derivative, which then reacts further with cyano-acetamide, forming the glutaric derivative. If this is the correct explanation, it is easy to understand the difference between the cyanoacetamide condensation and the Guareschi reaction, because, in the former case, it is to be anticipated that the addition of cyanoacetamide will lead to the more stable *trans*-configuration,

$$\begin{array}{cc} \mathrm{CN \cdot C \cdot CO \cdot NH_2} & \mathrm{CN \cdot CH \cdot CO \cdot NH_2} \\ \underset{\|}{\mathrm{R_2C}} \quad + \mathrm{NH_2 \cdot CO \cdot CH_2 \cdot CN} & \mathrm{R_2C} \\ & \mathrm{NH_2 \cdot CO \cdot CH \cdot CN} \end{array}$$
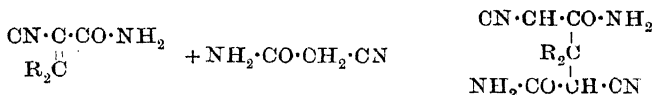
whereas in Guareschi's reaction the presence of excess of ammonia causes the production of the *cis*-derivative, owing to the tendency for the compound to pass into the ammonium salt,

$$\begin{array}{cc} \mathrm{CN \cdot CH \cdot CO \cdot NH_2} & \mathrm{CN \cdot CH \cdot C(ONH_4)} \\ \mathrm{R_2C} & \mathrm{R_2C \quad N} \\ \mathrm{NH_2 \cdot CO \cdot CH \cdot CN} & \mathrm{CN \cdot CH \cdot CO} \end{array}$$
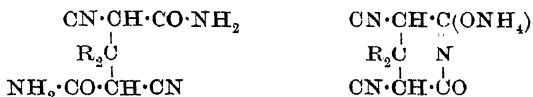
The latter is therefore an "enforced" reaction, and can, as will be shown, be made to yield condensation products in cases where a true catalytic reaction, such as the cyanoacetamide reaction, fails owing to a lack of tendency on the part of the ketone to yield a condensation product. It is found, for example, that the cyano-acetamide reaction can be effected with all ketones having two secondary carbon atoms next to the carbonyl group. If one of these is tertiary, the cyanoacetamide condensation fails, but products can be obtained by the Guareschi method, although in diminished yield. If both carbon atoms are tertiary, both the cyanoacetamide reaction and Guareschi's reaction fail to yield condensation products, and the same is the case if one carbon atom is quaternary, as in camphor and pinacolin.

We have been led to adopt this explanation of the course of the two reactions on account of the results of a series of experiments which have now been carried out on the question of the elimination of an alkyl group from the ortho-position during the condensation of ketones containing such groups with cyanoacetamide.

In Part XVIII (*loc. cit.*) it was noticed that 2-methyl*cyclo*hexanone (XV) and 2 : 4-dimethyl*cyclo*hexanone (XVI) gave with cyanoacetamide and piperidine the same condensation products as

those derived from *cyclo*hexanone and 4-methyl*cyclo*hexanone respectively:

$$CH_2{<}^{CH_2 \cdot CHMe}_{CH_2 — CH_2}{>}CO \qquad\qquad CHMe{<}^{CH_2 \cdot CHMe}_{CH_2 — CH_2}{>}CO$$
$$\text{(XV.)} \qquad\qquad\qquad\qquad \text{(XVI.)}$$

$$CH_2{<}^{CH_2 \cdot CHMe}_{CH_2 — CH_2}{>}C{<}^{CH(CN) \cdot CO}_{CH(CN) \cdot CO}{>}NH$$
$$\text{(XVII.)}$$
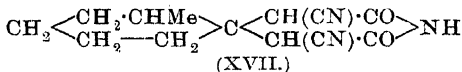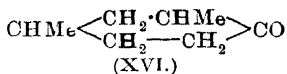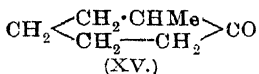
Great care was taken to purify these ketones, and although the yields of the condensation products were small and the reactions very sluggish, their constitutions were unquestionable. It was therefore assumed that the inhibiting effect of the ortho-methyl group prevented condensation, but that a certain portion of the ketone eliminated the inhibiting methyl group and yielded the product next lower in the series. At the same time, it was mentioned that Squintani (*Atti R. Accad. Sci. Torino*, 1912—1913, **48**, 675) had prepared from 2-methyl*cyclo*hexanone by the Guareschi method a condensation product melting at 210°, to which he assigned the structure XVI. It was also pointed out that the melting point of this substance was very close to that of the corresponding compound from *cyclo*hexanone, namely, 211—212°, and it was suggested that in this case also the ortho-methyl group had been eliminated.

The whole question has now been re-examined, and the pure *o*-methyl ketones have been regenerated from the carefully purified semicarbazones, with the result that it has been established beyond question that the ortho-substituted ketones do not react with cyanoacetamide, but give by the Guareschi method a poor yield of the ortho-substituted condensation product.

It follows also that the "pure" *o*-methyl ketones of Messrs. Poulenc contain appreciable quantities of the next lower homologue, which, curiously enough, cannot be detected either by analysis or by the precipitation of the semicarbazones, a fact that can be demonstrated in the following way. The "pure" 2-methyl*cyclo*hexanone of Messrs. Poulenc when treated with semicarbazide in slight excess was found to give a semicarbazone melting at 183—184°, in the crude condition, and at 190—191°, the correct melting point of the semicarbazone of 2-methyl*cyclo*hexanone, after being once recrystallised from alcohol (the semicarbazone of *cyclo*hexanone melts at 163°). A mixture of pure *cyclo*hexanone (15 per cent.) and pure 2-methyl*cyclo*hexanone (85 per cent.) was then made up, when it was found that a semicarbazone of the same melting point (183—184°) as that derived from the Poulenc
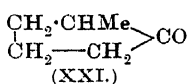
ketone was obtained. As a matter of fact, the presence of *cyclo*-hexanone could not be detected at all in this mixture. In the same way, the pure semicarbazone of 2:4-dimethyl*cyclo*hexanone (melting at 194°) was precipitated from the "pure" ketone of Messrs. Poulenc, although the presence in it of at least 10 per cent. of 4-methyl*cyclo*hexanone is clearly indicated by the experiments described in this paper.

Messrs. Poulenc informed us that this ketone must be free from 4-*cyclo*hexanone, because it is prepared by the Sabatier-Senderens process from *m*-4-xylenol. It is evident, however, that the ortho-methyl group is eliminated during the Sabatier-Senderens reduction, and not during the cyanoacetamide condensation. It is also evident that Squintani was dealing with a similar mixture of *cyclo*hexanone and 2-methyl*cyclo*hexanone, since the condensation product (XVII) prepared from the pure ortho-methyl ketone melts at 245°, and not at 210°. The structures of our products (XVII) and (XVIII) follows from the fact that they are completely converted into the acids (XIX) and (XX) on complete hydrolysis.

$$CHMe\begin{matrix}CH_2 \cdot CHMe \\ CH_2 \text{---} CH_2\end{matrix}>C<\begin{matrix}CH(CN) \cdot CO \\ CH(CN) \cdot CO\end{matrix}>NH$$
(XVIII.)

$$CHMe\begin{matrix}CH_2 \cdot CHMe \\ CH_2 \text{---} CH_2\end{matrix}>C<\begin{matrix}CH_2 \cdot CO_2H \\ CH_2 \cdot CO_2H\end{matrix}$$
(XX.)

$$CH_2\begin{matrix}CH_2 \cdot CHMe \\ CH_2 \text{---} CH_2\end{matrix}>C<\begin{matrix}CH_2 \cdot CO_2H \\ CH_2 \cdot CO_2H\end{matrix}$$
(XIX.)
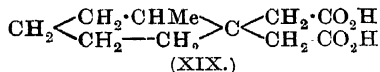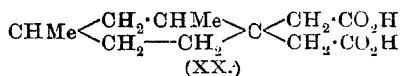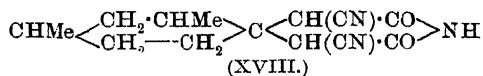
In order still further to emphasise the difference between the two types of reactions, we have investigated several other ketones having one tertiary carbon atom next to the carbonyl group. These compounds do not form condensation products with cyanoacetamide, but condense to a limited extent (the yield is usually about 15—20 per cent.) when subjected to the Guareschi reaction. These results may be summarised as follows.

2-Methyl*cyclo*pentanone (XXI) yields the condensation product (XXII), which is transformed into the acid (XXIII) on hydrolysis:

$$\begin{matrix}CH_2 \cdot CHMe \\ CH_2 \text{---} CH_2\end{matrix}>CO$$
(XXI.)

$$\begin{matrix}CH_2 \cdot CHMe \\ CH_2 \text{---} CH_2\end{matrix}>C<\begin{matrix}CH(CN) \cdot CO \\ CH(CN) \cdot CO\end{matrix}>NH$$
(XXII.)

$$\begin{matrix}CH_2 \cdot CHMe \\ CH_2 \text{---} CH_2\end{matrix}>C<\begin{matrix}CH_2 \cdot CO_2H \\ CH_2 \cdot CO_2H\end{matrix}$$
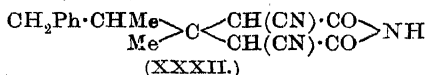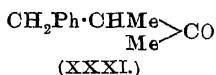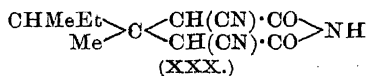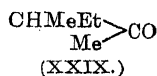(XXIII.)
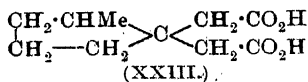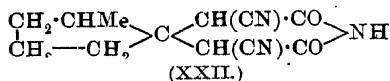
Dihydrocarvone (XXIV) gives a fairly good yield of the condensation product (XXV), which, however, cannot be hydrolysed without deep-seated decomposition.
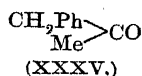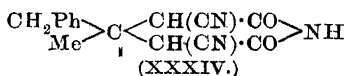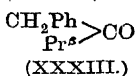
$$CH_2{\Large<}{}^{CH_2-------CHMe}_{CH(CMe{:}CH_2){\cdot}CH_2}{\Large>}CO$$
$$(XXIV.)$$

$$CH_2{\Large<}{}^{CH_2-------CHMe}_{CH(CMe{:}CH_2){\cdot}CH_2}{\Large>}C{\Large<}{}^{CH(CN){\cdot}CO}_{CH(CN){\cdot}CO}{\Large>}NH$$
$$(XXV.)$$
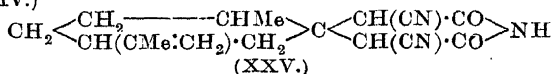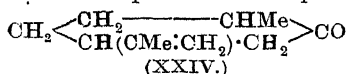
Methyl isopropyl ketone (XXVI) leads to the condensation product XXVII, which gives the acid XXVIII on hydrolysis:

$$^{Pr^\beta}_{Me}{\Large>}CO \qquad ^{Pr^\beta}_{Me}{\Large>}C{\Large<}^{CH(CN){\cdot}CO}_{CH(CN){\cdot}CO}{\Large>}NH \qquad ^{Pr^\beta}_{Me}{\Large>}C{\Large<}^{CH_2{\cdot}CO_2H}_{CH_2{\cdot}CO_2H}$$
$$(XXVI.) \qquad\qquad (XXVII.) \qquad\qquad\quad (XXVIII.)$$
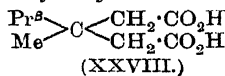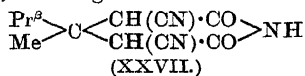
Methyl ψ-butyl ketone (XXIX) is converted into the product XXX, and benzylethyl methyl ketone (XXXI) into the compound XXXII :

$$^{CHMeEt}_{Me}{\Large>}CO \qquad\quad ^{CHMeEt}_{Me}{\Large>}C{\Large<}^{CH(CN){\cdot}CO}_{CH(CN){\cdot}CO}{\Large>}NH$$
$$(XXIX.) \qquad\qquad\qquad (XXX.)$$

$$^{CH_2Ph{\cdot}CHMe}_{Me}{\Large>}CO \qquad ^{CH_2Ph{\cdot}CHMe}_{Me}{\Large>}C{\Large<}^{CH(CN){\cdot}CO}_{CH(CN){\cdot}CO}{\Large>}NH$$
$$(XXXI.) \qquad\qquad\qquad (XXXII.)$$

The condensation of benzyl isopropyl ketone (XXXIII) with ethyl cyanoacetate and alcoholic ammonia has been described by Guareschi (*Gazzetta*, 1918, **48**, 97), who obtained a condensation product melting at 248°. We have repeated this condensation with the ketone supplied by Messrs. Poulenc, and have isolated both Guareschi's compound and also another which melts at 214—216°. The former we have identified as the benzylmethyl derivative (XXXIV) which we prepared from benzyl methyl ketone (XXXV):

$$^{CH_2Ph}_{Pr^\beta}{\Large>}CO \qquad ^{CH_2Ph}_{Me}{\Large>}C{\Large<}^{CH(CN){\cdot}CO}_{CH(CN){\cdot}CO}{\Large>}NH \qquad ^{CH_2Ph}_{Me}{\Large>}CO$$
$$(XXXIII.) \qquad\qquad (XXXIV.) \qquad\qquad\qquad (XXXV.)$$

The latter was found to be identical with the benzylethyl derivative (XXXVI) prepared in a similar manner from pure benzyl ethyl ketone (XXXVII):

$$^{CH_2Ph}_{Et}{\Large>}C{\Large<}^{CH(CN){\cdot}CO}_{CH(CN){\cdot}CO}{\Large>}NH \qquad ^{CH_2Ph}_{Et}{\Large>}CO$$
$$(XXXVI.) \qquad\qquad\qquad (XXXVII.)$$

$$^{CH_2Ph}_{Pr^\beta}{\Large>}C{\Large<}^{CH(CN){\cdot}CO}_{CH(CN){\cdot}CO}{\Large>}NH$$
$$(XXXVIII)$$
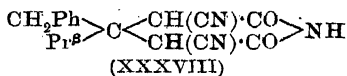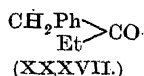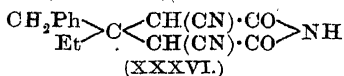
It is evident, therefore, that the benzyl *iso*propyl ketone used by Guareschi and by us contained considerable quantities of benzyl ethyl and benzyl methyl ketones. In order to settle this point, we prepared the pure benzyl *iso*propyl ketone by distilling a mixture of the calcium salts of phenylacetic and *iso*butyric acids in accordance with Ludlam's method (T., 1902, **81**, 1185). The purity of the ketone was controlled by the formation of the semicarbazone, which we found to melt at 138—139°, in agreement with the figure found by Blaise (*Compt. rend.*, 1901, **132**, 480), and not at 126°, the number given by Senderens (*Compt. rend.*, 1910, **150**, 1138).

When condensed with ethyl cyanoacetate by the Guareschi method, no trace of the condensation product (XXXVIII) could be isolated, and it would appear, therefore, that the occurrence of these lower homologues in commercial benzyl *iso*propyl ketone is another example of the elimination of ortho-alkyl groups.

Some of the acids formed from these condensation products on hydrolysis appear to be abnormal, and a description of them is therefore reserved for a future communication.

Experimental.

The condensation of ketones with cyanoacetamide was carried out in the manner already described (T., 1911, **99**, 424). For the condensations with ethyl cyanoacetate, Guareschi's instructions were, in the main, followed. The ketone (one molecular proportion) was mixed with ethyl cyanoacetate (two molecular proportions), and a little more than three molecular proportions of ammonia, dissolved in absolute methyl or ethyl alcohol, added to the mixture. The solution assumed a yellow or orange colour and became warm. It was kept at 40° for forty-eight hours, by which time the ammonium salt of the dicyanopiperidine derivative had separated; in many instances, some cyanoacetamide was precipitated at the same time. In all cases, sufficient water was added to dissolve the salt, the solution extracted with ether to remove unchanged ketone, and the extracted solution acidified, when the dicyanopiperidine was precipitated, usually in several crops. All the compounds of this type were found to be colourless and to crystallise remarkably well.

2-*Methyl*cyclo*hexanone* (XV, p. 690).

This ketone, when carefully purified by regenerationg it from the pure semicarbazone, does not condense with cyanoacetamide, the latter being recovered unchanged.

With ethyl cyanoacetate and alcoholic ammonia, the commercial preparations of the ketone give mixtures containing varying quantities of two compounds, one melting at 207° and the other at 245°. They can be separated by a tedious process of fractional crystallisation from 50 per cent. aqueous alcohol; the compound of higher melting point is the less soluble and crystallises out first, but mixtures of various melting points, ranging from 190° to 210°, are obtained intermediately, and this probably accounts for the results obtained by Squintani (see p. 690).

The compound melting at 207° was identified by direct comparison and by analysis (Found: C = 62·28; H = 5·79. $C_{12}H_{13}O_2N_3$ requires C = 62·3; H = 5·6 per cent.) as the ω-imide of aa'-dicyano-*cyclo*hexane-1:1-diacetic acid, $C_5H_{10}{:}C{<}^{CH(CN)\cdot CO}_{CH(CN)\cdot CO}{>}NH$ (compare Thorpe and Wood, T., 1913, **103**, 1592). On hydrolysis with 60 per cent. sulphuric acid, it yielded *cyclo*hexane-1:1-diacetic acid, melting at 181°, which was identified by direct comparison with a specimen prepared from *cyclo*hexanone.

The compound melting at 245° is the sole product of the reaction if the ketone used is absolutely pure; the yield is about 3 grams from 11·2 grams of the ketone.

The *ω-imide* of aa'-*dicyano*-2-*methyl*cyclohexane-1:1-*diacetic acid* (XVII, p. 690) crystallises from 50 per cent. aqueous alcohol in glistening plates and melts at 245° with slight decomposition:

0·1016 gave 0·2375 CO_2 and 0·0557 H_2O. C = 63·80; H = 6·09.

0·1182 ,, 17·7 c.c. N_2 at 19° and 766 mm. N = 17·34.

$C_{13}H_{15}O_2N_3$ requires C = 63·7; H = 6·1; N = 17·1 per cent.

The *ω-imide* of aa'-*dicarbamyl*-2-*methyl*cyclohexane-1:1-*diacetic acid*, $CH_2{<}^{CH_2\cdot CHMe}_{CH_2{-}CH_2}{>}C{<}^{CH(CO\cdot NH_2)\cdot CO}_{CH(CO\cdot NH_2)\cdot CO}{>}NH$, is obtained as a microcrystalline precipitate when the above dicyano-derivative is dissolved in ten times its weight of concentrated sulphuric acid and the solution, after keeping for twenty-four hours at the ordinary temperature, is poured into ice-water. It crystallises from absolute alcohol in small plates, which melt and decompose at 275°:

0·1357 gave 0·2735 CO_2 and 0·0828 H_2O. C = 54·96; H = 6·78.

0·1583 ,, 21 c.c. N_2 at 21° and 755 mm. N = 14·94.

$C_{13}H_{19}O_4N_3$ requires C = 55·5; H = 6·8; N = 14·9 per cent.

2-*Methyl*cyclohexane-1:1-*diacetic acid* (XIX, p. 691) is formed in excellent yield when the dicyano-derivative is hydrolysed by 60 per cent. sulphuric acid in accordance with the method described by Thole and Thorpe (T., 1911, **99**, 434). It crystallises from dilute alcohol in colourless, iridescent plates, or from benzene,

in which it is sparingly soluble, in prismatic needles. Both forms melt at 148°:

0·1088 gave 0·2462 CO_2 and 0·0816 H_2O. C=61·70; H=8·33.

$C_{11}H_{18}O_4$ requires C=61·7; H=8·4 per cent.

A normal solution of the neutral ammonium salt of the acid does not give a precipitate with either barium or calcium chlorides, but if more concentrated solutions are used, a copious precipitate of the calcium salt can be obtained on boiling. The *silver* salt is a white, curdy precipitate:

0·1266 gave 0·0634 Ag. Ag=50·05.

$C_{11}H_{16}O_4Ag_2$ requires Ag=50·45 per cent.

Neither the anhydride nor the semianilide of this acid could be obtained in a crystalline condition, although the former can be readily prepared as an oil, insoluble in aqueous sodium hydrogen carbonate solution, by treating the acid with hot acetyl chloride.

2 : 4-*Dimethyl*cyclo*hexanone* (XVI, p. 690).

The pure ketone, regenerated from the semicarbazone, does not condense with cyanoacetamide. Commercial preparations of the ketone readily condense with ethyl cyanoacetate, 12·6 grams of the ketone giving about 3·2 grams of a crude condensation product melting at 205—210°.

On recrystallisation from alcohol, a small amount of a substance crystallising in needles and melting at 213° is obtained from the more soluble portion. This substance was identified as the ω-imide of αα'-dicyano-4-methyl*cyclo*hexane-1 : 1-diacetic acid,

$$CHMe\underset{CH_2 \cdot CH_2}{\overset{CH_2 \cdot CH_2}{<}} C \underset{CH(CN) \cdot CO}{\overset{CH(CN) \cdot CO}{<}} NH,$$
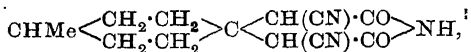
by direct comparison with a specimen prepared from 4-methyl-*cyclo*hexanone. The bulk of the product consists of the *ω-imide* of *αα'-dicyano-2 : 4-dimethylcyclohexane-1 : 1-diacetic acid* (XVIII, p. 691), which crystallises from alcohol in sparkling plates melting at 236°, not unlike the 2-methyl compound in appearance:

0·1254 gave 0·2970 CO_2 and 0·0751 H_2O. C=64·60; H=6·65.

$C_{14}H_{17}O_2N_3$ requires C=64·9; H=6·6 per cent.

2 : 4-*Dimethyl*cyclo*hexane*-1 : 1-*diacetic acid* (XX, p. 691) is obtained in good yield when the above dicyano-imide is hydrolysed with 60 per cent. sulphuric acid. It crystallises from water containing a little alcohol in long, prismatic needles melting at 152°, and is very sparingly soluble in benzene:

0·1180 gave 0·2730 CO_2 and 0·0935 H_2O.   C=63·10; H=8·80.

$C_{12}H_{20}O_4$ requires C=63·2; H=8·8 per cent.

2:4-*Dimethyl*cyclo*hexane*-1:1-*diacetic anhydride*,

$$CHMe \begin{matrix} CH_2 \cdot CHMe \\ CH_2 \!-\! CH_2 \end{matrix} \Big\rangle C \begin{matrix} CH_2 \cdot CO \\ CH_2 \cdot CO \end{matrix} \Big\rangle O,$$
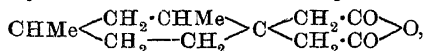
which can be obtained by boiling the acid with acetyl chloride, crystallises from light petroleum (b. p. 60—80°), containing a little benzene, in colourless plates melting at 68·5°:

0·1173 gave 0·2959 CO_2 and 0·0918 H_2O.   C=68·77; H=8·70.

$C_{12}H_{18}O_3$ requires C=68·6; H=8·6 per cent.

The *semianilide*, prepared in the usual manner from a benzene solution of the anhydride and aniline, crystallises from dilute alcohol in glistening laminæ melting at 151°:

0·1095 gave 0·2850 CO_2 and 0·0820 H_2O.   C=70·97; H=8·13.

$C_{18}H_{25}O_3N$ requires C=71·3; H=8·3 per cent.

Dihydrocarvone (XXIV, p. 692).

The ketone was prepared by the reduction of carvone by zinc dust and sodium hydroxide (Wallach, *Annalen*, 1894, **279**, 377). It does not combine with cyanoacetamide, but condenses fairly readily with ethyl cyanoacetate, the yield of condensation product being about 3 grams from 15·2 grams of the ketone. Care should be taken to remove the unchanged ketone by repeated extraction with ether, otherwise the condensation product is difficult to purify. The sole product of the reaction is the *ω-imide* of *αα'-dicyano*-2-*methyl*-5-iso*propylidenecyclohexane*-1 : 1-*diacetic acid* (XXV, p. 692), which separates from dilute alcohol in clusters of silky needles melting at 198—199°, but sintering and darkening at 197°:

0·1091 gave 0·2698 CO_2 and 0·0667 H_2O.   C=67·61; H=6·79.

0·1131   ,,   0·2782 CO_2 ,,   0·0688 H_2O.   C=67·05; H=6·76.

0·0860   ,,   10·8 c.c. N_2 at 14·5° and 774·5 mm.   N=15·00.

$C_{16}H_{19}O_2N_3$ requires C=67·4; H=6·7; N=14·7 per cent.

Several attempts were made to hydrolyse this compound to the corresponding non-nitrogenous acid, but a deep-seated decomposition appeared to take place, and we were unable to isolate any crystalline product.

2-*Methyl*cyclo*pentanone* (XXI, p. 691).

This compound was prepared by the hydrolysis of the corresponding carboxylic ester with dilute sulphuric acid, according to

Dieckmann's method (*Annalen*, 1901, **317**, 27). It does not combine with cyanoacetamide, and only gives a very poor yield of condensation product with ethyl cyanoacetate. This consists of the *ω-imide* of *αα'-dicyano-2-methyl*cyclo*pentane-*1:1-*diacetic acid* (XXII, p. 691), which crystallises from alcohol in glistening plates melting at 237°:

0·0943 gave 0·2109 CO_2 and 0·0484 H_2O.   C = 62·40 ; H = 5·70.
$C_{12}H_{13}O_2N_3$ requires C = 62·3 ; H = 5·6 per cent.

*2-Methyl*cyclo*pentane-*1:1-*diacetic acid* (XXIII, p. 691) is obtained from the above dicyano-imide on hydrolysing it with 60 per cent. aqueous sulphuric acid. It crystallises from a mixture of benzene and light petroleum (b. p. 60—80°) in small prisms melting at 112°:

0·1361 gave 0·3010 CO_2 and 0·0998 H_2O.   C = 60·33 ; H = 8·15.
$C_{10}H_{16}O_4$ requires C = 60·0 ; H = 8·0 per cent.

cyclo*Pentanone.*

The greater part of the ketone required was prepared by distilling adipic acid with a small quantity of baryta (D.R.-P., Appl. F.33624). The method gives a yield far superior to that obtained by the dry distillation of calcium adipate or by Blanc's method involving the use of acetic anhydride.

Condensation with Cyanoacetamide.—cyclo Pentanone reacts in this condensation differently from cyclohexanone and its derivatives, owing, presumably, to the greater solubility of the normal condensation product. If the operation is carried out at the ordinary temperature, very little of the imino-compound is formed even if an excess of cyanoacetamide is used. The main product is the amide of *α-cyano-Δ¹-*cyclo*penteneacetic acid* (XII, p. 688), which separates in several crops, usually in rhombohedral crystals. The yield is about 6 grams from 25 grams of cyanoacetamide. A little imino-compound (melting at 287°, see p. 688) also separates in the later stages, and on acidifying the mother liquor, some diimide (see p. 688) is obtained. The amide possesses a remarkable tendency to crystallise, and can be recrystallised from almost any of the usual solvents. It separates from water in magnificent, long needles, closely resembling phthalic anhydride in appearance. From alcohol, in which it is freely soluble, rhombohedral aggregates are obtained. Similar crystals separate from ethyl acetate, whereas from chloroform, benzene, or light petroleum the compound crystallises in needles. It melts at 134°:

D D* 2

0·1257 gave 0·2949 CO_2 and 0·0756 H_2O.   C = 63·98; H = 6·68.

0·1318 „ 21·5 c.c. N_2 at 13° and 755·5 mm.   N = 18·93.

$C_8H_{10}ON_2$ requires C = 64·0; H = 6·7; N = 18·7 per cent.

On prolonged boiling with water, and especially dilute alkali, ammonia and some *cyclo*pentanone are evolved. On acidifying and extracting with ether, an acid is obtained melting at 130—131°. This acid is, however, more conveniently prepared by dissolving the amide (1 gram) in concentrated sulphuric acid (5 c.c.) and slowly adding 6 c.c. of a 20 per cent. sodium nitrite solution to the ice-cold mixture, the reaction being completed by warming on the water-bath for half an hour. On cooling, the solution deposits the acid in thin, felted needles, which, after recrystallisation from a mixture of benzene and light petroleum, melt at 130—131° (Found: C = 63·70; H = 6·18; N = 9·57. $C_8H_9O_2N$ requires C = 63·6; H = 6·0; N = 9·3 per cent.). The acid is evidently identical with α-cyano-Δ1-*cyclo*penteneacetic acid (XII, p. 688) obtained by Harding and Haworth (T., 1910, **97**, 486).

If the condensation of *cyclo*pentanone with cyanoacetamide is effected at a higher temperature and care is taken to prevent the precipitation of the amide by adding more alcohol, the reaction proceeds a step further. Thus when 14 grams of cyanoacetamide are dissolved in 50 c.c. of water, 7 c.c. of *cyclo*pentanone, 50 c.c. of alcohol, and a few drops of piperidine added, the liquid, after being kept for some time at 37°, deposits a microcrystalline solid, melting and decomposing at 287°, which is completely soluble in dilute mineral acids, and appears to be the ω-*di-iminodi-imide* of cyclo*pentane*-1:1-*dimalonic acid* (XIV, p. 688). The yield of this substance is, however, poor, and the condensation is not to be recommended for the preparation of the corresponding diacetic acid. Much of the imino-compound remains in solution, and separates on acidifying as the di-imide (see below). The formation of the acid by-product (the dicyano-imide) was not observed.

A similar result is obtained when an alcoholic solution of cyanoacetamide (one molecule) and the amide of α-cyano-Δ1-*cyclo*penteneacetic acid (p. 688) is mixed with a few drops of piperidine and allowed to remain at 40°. A small amount of the imino-compound (XIV, p. 688) is deposited first, and, on acidifying, the di-imide separates.

The di-iminodi-imide (XIV, p. 688) is soluble in dilute mineral acids, and separates again if the solution is immediately poured into aqueous sodium acetate, but even then a partial hydrolysis of the imino-groups occurs, and concordant figures could not be obtained on analysis. For the same reason, the platinichloride could not be prepared uncontaminated with ammonium platini-

chloride. The specimen for analysis was therefore purified by washing, and the analytical figures lead to the formula $C_{11}H_{14}O_2N_4 + \frac{1}{2}H_2O$, but it must be remembered that the compounds of this type burn only with the greatest difficulty:
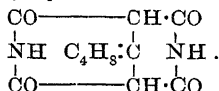
0·1590 gave 0·3177 CO_2 and 0·0920 H_2O. C=54·50; H=6·43.

0·1125 ,, 0·2255 CO_2 ,, 0·0647 H_2O. C=54·67; H=6·39.

0·1535 ,, 29·8 c.c. N_2 at 8·5° and 760 mm. N=23·36.

$C_{11}H_{14}O_2N_4 + \frac{1}{2}H_2O$ requires C=54·3; H=6·2; N=23·1 per cent.

The ω-Di-imide of cyclo*Pentane*-1 : 1-*dimalonic Acid,*

$$\begin{array}{ccc} CO & \! CH\cdot CO & \\ NH & C_4H_8{:}C & NH \\ CO & \! CH\cdot CO & \end{array}.$$

This compound is obtained on acidifying the mother liquors from which the di-imino-compound has been filtered off, or by boiling the latter with dilute hydrochloric acid for a short time. It can be produced in a variety of crystalline forms—usually in fern-shaped aggregates of prisms—if allowed to separate slowly from the original liquors. When recrystallised from much alcohol or glacial acetic acid, it is obtained in small, silvery plates which decompose without melting at about 360°:
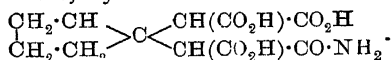
0·1282 gave 0·2608 CO_2 and 0·0616 H_2O. C=55·48; H=5·34.

0·1814 ,, 18·2 c.c. N_2 at 8° and 757 mm. N=12·03.

$C_{11}H_{12}O_4N_2$ requires C=55·9; H=5·1; N=11·9 per cent.

The di-imide slowly dissolves in sodium carbonate solution, but is sparingly soluble in all organic solvents.

The Amide of cyclo*Pentane*-1 : 1-*dimalonic Acid,*

$$\begin{array}{c} CH_2\cdot CH \\ CH_2\cdot CH_2 \end{array}\!\!\!>\!C\!<\!\!\!\begin{array}{c} CH(CO_2H)\cdot CO_2H \\ CH(CO_2H)\cdot CO\cdot NH_2 \end{array}.$$

When either the above di-imide or the dicyano-imide (see below) is boiled with a slight excess of 20 per cent. aqueous potassium hydroxide for not longer than three-quarters of an hour, the solution deposits this amido-acid as a crystalline precipitate when acidified. It can be recrystallised from water, and melts with vigorous decomposition at 157°:

0·1636 gave 0·2907 CO_2 and 0·0819 H_2O. C=48·46; H=5·56.

$C_{11}H_{17}O_7N$ requires C=48·4; H=5·5 per cent.

0·1647 required 18·20 c.c. of $N/10$-NaOH for neutralisation.
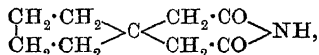
$C_{11}H_{17}O_7N$ (tribasic) requires ·18·10 c.c.

cyclo*Pentane*-1:1-*dimalonic Acid*, $\begin{matrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{matrix} > C < \begin{matrix} CH(CO_2H)_2 \\ CH(CO_2H)_2 \end{matrix}$.—

When a solution of the above amido-acid in an excess of 10 per cent. sodium hydroxide solution is boiled until no more ammonia is evolved, and the solution is acidified, the above acid separates. It crystallises from hydrochloric acid in plates, which decompose at 169° into carbon dioxide and cyclo*pentane*-1:1-*diacetic acid*:

0·1062 gave 0·1872 CO_2 and 0·0510 H_2O.   C = 48·10; H = 5·34.

$C_{11}H_{14}O_8$ requires C = 48·2; H = 5·1 per cent.

The *imide* of cyclo*pentane*-1:1-*diacetic acid*,

$$\begin{matrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{matrix} > C < \begin{matrix} CH_2 \cdot CO \\ CH_2 \cdot CO \end{matrix} > NH,$$

is prepared by heating the amido-tricarboxylic acid at a temperature a few degrees above its melting point until the evolution of carbon dioxide has ceased. It crystallises from water in glistening plates melting at 153°:

0·1139 gave 0·2705 CO_2 and 0·0805 H_2O.   C = 64·77; H = 7·85.

0·1652 „ 13·0 c.c. N_2 at 26·5° and 760·3 mm.   N = 8·68.

$C_9H_{13}O_2N$ requires C = 64·7; H = 7·8; N = 8·4 per cent.

cyclo*Pentane*-1:1-*diacetic   acid*, $\begin{matrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{matrix} > C < \begin{matrix} CH_2 \cdot CO_2H \\ CH_2 \cdot CO_2H \end{matrix}$, is

obtained in excellent yield when either the imino-compound or the di-imide are hydrolysed with sulphuric acid in the usual way. The acid crystallises from water in fern-shaped aggregates of prismatic needles melting at 176—177°. It is sparingly soluble in benzene:

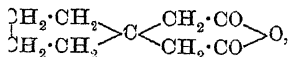0·1371 gave 0·2910 CO_2 and 0·0920 H_2O.   C = 57·89; H = 7·46.

$C_9H_{14}O_4$ requires C = 58·1; H = 7·5 per cent.

A normal solution of the neutral ammonium salt of the acid gives no precipitate with barium chloride either in the cold or on boiling.   On boiling with normal calcium chloride solution, a white precipitate is formed, which does not redissolve on cooling. The *silver* salt is a white, curdy precipitate, which slowly darkens on exposure to light:

0·2149 gave 0·1159 Ag.   Ag = 53·84.

$C_9H_{12}O_4Ag_2$ requires Ag = 54·0 per cent.

cyclo*Pentane*-1:1-*diacetic anhydride*,

$$\begin{matrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{matrix} > C < \begin{matrix} CH_2 \cdot CO \\ CH_2 \cdot CO \end{matrix} > O,$$

is obtained when the acid is boiled with an excess of acetic anhydride or acetyl chloride, and crystallises as the reagent

evaporates. It separates from light petroleum (b. p. 60—80°) containing a little benzene in iridescent laminæ melting at 68°:

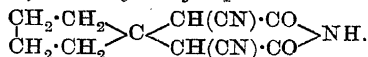0·1528 gave 0·3586 CO_2 and 0·0936 H_2O. C=64·02; H=6·81.
$C_9H_{12}O_3$ requires C=64·3; H=7·0 per cent.

The *semianilide* is readily obtained on boiling the anhydride and aniline in benzene solution. It crystallises from alcohol in large, colourless laminæ melting at 118°:

0·1127 gave 0·2852 CO_2 and 0·0730 H_2O. C=69·03; H=7·20.
$C_{15}H_{19}O_3N$ requires C=69·0; H=7·3 per cent.

The ω-Imide of αα′-Dicyanocyclopentane-1 : 1-diacetic Acid,

$$\begin{array}{c} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{array}\!\!>\!\!C\!\!<\!\!\begin{array}{c} CH(CN) \cdot CO \\ CH(CN) \cdot CO \end{array}\!\!>\!\!NH.$$

This compound is obtained when *cyclo*pentanone is condensed with ethyl cyanoacetate in the presence of alcoholic ammonia, the yield being about 50 per cent. of the theoretical. As a good yield of *cyclo*pentane-1 : 1-diacetic acid can be easily obtained from the dicyano-imide on hydrolysis, this condensation is the best means for preparing the acid in quantity. The imide crystallises from dilute alcohol in stellate clusters of needles melting at 179—180°:

0·1588 gave 0·3531 CO_2 and 0·0717 H_2O. C=60·63; H=5·02.
$C_{11}H_{11}O_2N_3$ requires C=60·8; H=5·1 per cent.

The ω-*imide* of αα′-*dicarbamyl*cyclopentane-1 : 1-*diacetic acid*,

$$C_4H_8:C\!\!<\!\!\begin{array}{c} CH(CO \cdot NH_2) \cdot CO \\ CH(CO \cdot NH_2) \cdot CO \end{array}\!\!>\!\!NH,$$ is formed from the dicyano-

derivative when it is treated with cold, concentrated sulphuric acid. It crystallises from much alcohol in small, colourless prisms, which darken at 285° and carbonise without melting at 310°:

0·1166 gave 0·2219 CO_2 and 0·0631 H_2O. C=51·88; H=6·01.
0·1620   23·4 c.c. N_2 at 15·5° and 751·5. N=16·62.
$C_{11}H_{15}O_4N_3$ requires C=52·2; H=5·9; N=16·6 per cent.

Complete hydrolysis of the above compounds with 60 per cent. sulphuric acid leads to *cyclo*pentane-1 : 1-diacetic acid.

Methyl isoPropyl Ketone (XXVI, p. 692).

This ketone does not condense with cyanoacetamide. The condensation with ethyl cyanoacetate has already been carried out by Guareschi (*Atti R. Accad. Sci. Torino*, 1901, **50**, 288), but he did not analyse the product.

We find that 8·6 grams of the ketone when treated with 22·6

grams of ethyl cyanoacetate and 50 c.c. of alcoholic ammonia (12 per cent.) give 3·2 grams of the condensation product, which is the *ω-imide* of *αα'-dicyano-β-methyl-β-*iso*propylglutaric acid* (XXVII, p. 692). It crystallises from alcohol in lustrous plates which melt at 233—234°:

0·1271 gave 0·2815 CO_2 and 0·0656 H_2O.   C = 60·40; H = 5·74.
0·1603   ,,   26·1 c.c. N_2 at 9° and 756 mm.   N = 19·40.
$C_{11}H_{13}O_2N_3$ requires C = 60·3; H = 5·9; N = 19·2 per cent.

*β-Methyl-β-*iso*propylglutaric acid* (XXVIII, p. 692) is produced when the above imide is hydrolysed with 60 per cent. sulphuric acid. It crystallises from benzene in small plates melting at 100°:

0·1315 gave 0·2761 CO_2 and 0·0994 H_2O.   C = 57·26; H = 8·40.
$C_9H_{16}O_4$ requires C = 57·4; H = 8·5 per cent.

*β-Methyl-β-*iso*propylglutaric anhydride,* $\mathrm{Me}^{\mathrm{Pr^8}}\!\!>\!\!C\!<^{CH_2\cdot CO}_{CH_2\cdot CO}\!\!>\!\!O,$

is prepared by boiling the acid for a short time with acetyl chloride. It crystallises from light petroleum (b. p. 60—80°) mixed with a small quantity of the same solvent boiling at 80—100° in glistening plates melting at 41—42°:

0·1181 gave 0·2740 CO_2 and 0·0880 H_2O.   C = 63·28; H = 8·28.
    $C_9H_{14}O_3$ requires C = 63·5; H = 8·2 per cent.

Methyl ψ-Butyl Ketone (XXIX, p. 692).

This ketone was prepared by the hydrolysis of ethyl methylethylacetoacetate according to the directions of Wislicenus (*Annalen*, 1883, **219**, 303). It does not condense with cyanoacetamide, but gives with ethyl cyanoacetate a very small yield of the *ω-imide* of *αα'-dicyano-β-methyl-β-ψ-butylglutaric acid* (XXX, p. 692), a substance which crystallises from alcohol in magnificent, nacreous plates resembling naphthalene in appearance, and melting at 215—216°:

0·0827 gave 0·1860 CO_2 and 0·0471 H_2O.   C = 61·33; H = 6·33.
0·0553   ,,   8·65 c.c. N_2 at 16·5° and 770 mm.   N = 18·36.
 $C_{12}H_{15}O_2N_3$ requires C = 61·8; H = 6·44; N = 18·0 per cent.

Benzylethylmethyl Ketone (XXXI p. 692).

The ketone required for this investigation was prepared according to Harries and Müller's method (*Ber.*, 1902, **35**, 966). The yield of condensation product with ethyl cyanoacetate and

alcoholic ammonia was found to be exceedingly small—0·5 gram being obtained from 8·1 grams of the ketone. The ω-*imide* of *αα'-dicyano-β-methyl-β-(α-benzylethyl)glutaric acid* (XXXII, p. 692) crystallises from dilute alcohol in small needles melting at 223—224°:

0·1212 gave 0·3068 CO_2 and 0·0636 H_2O. C = 69·05; H = 5·83.
$C_{17}H_{17}O_2N_3$ requires C = 69·2; H = 5·8 per cent.

Benzyl iso*Propyl Ketone* (XXXIII, p. 692).

The pure ketone was prepared by distilling together an intimate mixture of calcium phenylacetate and calcium *iso*butyrate in a current of carbon dioxide. The product was fractionated and separated into three main fractions, consisting of di*iso*propyl ketone, benzyl *iso*propyl ketone, and dibenzyl ketone. After refractionation, 30 grams of benzyl *iso*propyl ketone were obtained from 165 grams of calcium phenylacetate. The ketone boils at 238—240°. The *semicarbazone* is formed when a solution of semicarbazide acetate is mixed with the ketone, together with enough alcohol to bring the latter into solution, and the mixture allowed to remain overnight. It crystallises from alcohol in small, cubical crystals resembling common salt, and melts at 138° to a colourless, opaque liquid, which clears at 139°:

0·1454 gave 25·8 c.c. N_2 at 28° and 762·4 mm. N = 19·38.
$C_{12}H_{17}ON_3$ requires N = 19·2 per cent.

No condensation product could be obtained from this ketone either with cyanoacetamide or with ethyl cyanoacetate.

When a commercial preparation of the ketone was employed, a condensation product was obtained in poor yield; from this, two compounds were isolated by fractional crystallisation from alcohol. One of these crystallised in clusters of prismatic needles melting at 214—216°, and was proved by direct comparison to be identical with the benzylethyl compound (*q.v.*) (Found: C = 68·21; H = 5·36; N = 15·17. $C_{16}H_{15}O_2N_3$ requires C = 68·3; H = 5·3; N = 14·9 per cent.).

The other compound can be obtained from the mother liquors after the above compound has separated out, although, with one sample of the ketone, it formed the greater part of the condensation product. It crystallised from alcohol in long, flattened needles melting at 246—247°, and was proved by direct comparison to be identical with the benzylmethyl compound (*q.v.*) (Found: C = 67·53; H = 5·09. $C_{15}H_{13}O_2N_3$ requires C = 67·4; H = 4·9 per

cent.).   This compound appears to be identical with the one described by Guareschi as the benzyl*iso*propyl derivative (*Gazzetta*, 1918, **48**, 97).

Benzyl Ethyl Ketone (XXXVII, p. 692).

A condensation product with ethyl cyanoacetate was readily obtained from this ketone, and was prepared for the sake of comparing it with that obtained from benzyl *iso*propyl ketone. We find the yield to be as high as 7·5 grams from 14·8 grams of the ketone (compare Guareschi, *Gazzetta*, 1918, **48**, 92).

The *ω-imide* of *αα'-dicyano-β-benzyl-β-ethylglutaric   acid* (XXXVI, p. 692) crystallises from alcohol in fine, prismatic needles melting at 214—216° (Guareschi, *loc. cit.*, gives 222—226° as the melting point of this substance):

0·1192 gave 0·2984 CO_2 and 0·0566 H_2O.   C=68·27; H=5·28.

$C_{16}H_{15}O_2N_3$ requires C=68·3; H=5·3 per cent.

The products obtained by the acid hydrolysis of this imide appear to be abnormal, and are still under investigation.

Benzyl Methyl Ketone (XXXV, p. 692).

This ketone condenses very readily with ethyl cyanoacetate and gives a good yield (13 grams from 10 grams of the ketone) of the *ω-imide* of *αα'-dicyano-β-benzyl-β-methylglutaric acid* (XXXIV, p. 692). It crystallises from alcohol in long, flattened needles, which melt at 246—247° and decompose a few degrees above this temperature:

0·1194 gave 0·2938 CO_2 and 0·0506 H_2O.   C=67·12; H=4·71.

0·1072   ,,   0·2650 CO_2 (by CrO_3 method).   C=67·40.

$C_{15}H_{13}O_2N_3$ requires C=67·4; H=4·9 per cent.

THE IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON.   [*Received, June 3rd*, 1919.]

LVIII.—"*Blue John*" *and other Forms of Fluorite.*

By BERTRAM BLOUNT and JAMES HARRY SEQUEIRA.

A GOOD deal of work has been done on the properties of fluorspar or fluorite in the various forms in which it occurs in nature. Fluorspar as an industrial substance is ably dealt with in a memoir of the Geological Survey, entitled "Special Reports on the Mineral Resources of Great Britain," by Messrs. Carruthers, Pocock, and May, to which Messrs. Dewey and Brownhead have contributed. In this pamphlet, no reference is made to the cause of the colour.

Derbyshire is properly regarded as the home of "Blue John." The famous Blue John mine is in the Castleton district, and is thus described. "The Blue John mine consists of a number of natural caverns in carboniferous limestone connected by tortuous pipes or fissures and extending for a great distance. The blue fluorspar or 'Blue John' occurs as a lining on the walls of fissures and pipes, or in concentrically arranged layers. It is associated with barytes, and a leader of this mineral is usually considered a good guide to a deposit of 'Blue John.' The so-called veins are irregular, flattened pipes running for a while almost horizontally, and then bending sharply up and down and cutting across the bedding. Where a vein is nearly flat, its upper and lower surfaces are lined by coatings of blue fluorspar. . . ." This is enough for the present purpose, and it may be accepted that this is the best account extant of the occurrence of "Blue John" in Great Britain.

There is not much that we have been able to discover in foreign literature except a paper by H. W. Morse (*Proc. Amer. Acad. Arts and Sci.*, 1906), which deals chiefly with the fluorescence of fluorite as studied in the spectroscope, but incidentally touches on some points of interest here. The essential statements are that the cause of the colour may be due to organic matter, and the conclusion arrived at is that "the question as to the cause of the colour of fluorspar still remains in this unsettled state." It is further said that the cause of the odour on heating is doubtful, and, further, that the gases expelled by this means are chiefly carbon dioxide, carbon monoxide, and hydrogen. Tests were made for helium on 10 kilos. of fluorite with a negative result, and the author of the paper feels so doubtful of his conclusion that towards the end of his paper he says: "I saw no reason to question the statement that the colour of fluorite is due to organic matter."

The evidence for and against this view is given in the ensuing notes of experiments made by ourselves.

Chemical Composition of Blue John.

Below are analysis of "Blue John" and of the white parts of the same mineral.

	"Blue John." Per cent.	White portions of same sample. Per cent.
Calcium fluoride	99·69	99·71
Alumina and ferric oxide	0·048	0·026
Manganese	nil	nil
Magnesia	0·006	0·005
Chlorine	nil	nil
Sulphur trioxide	nil	nil
Sulphur	trace	trace
Phosphorus	0·09	0·08

It will be seen that the difference between them is so small as to be almost inappreciable. It will also be noticed that metals such as manganese, which have been regarded as likely to be the cause of the colour, are practically absent.

The natural conclusion is that the colour of "Blue John" is due to some organic dye of animal origin, and that this has been absorbed by certain parts of the "Blue John" as distinct from others. Some support is given to this idea by the fact that there is usually a mechanical line of demarcation between the white and blue portions of typical pieces of "Blue John." This assumption of the cause of colour was tested by systematic extraction of "Blue John," powdered so as to pass a 60×60 mesh sieve, with chloroform, toluene, and aniline. Chloroform extracted 0·11 per cent. of oily matter, toluene 0·04 per cent. of a similar substance, and aniline nothing further. Acetone, nitrobenzene, and naphthalene were also tried, with negative results; the extracted mineral remained as deep a blue as before extraction. A combustion of the extracted material gave $C = 0·046$ per cent., showing that the amount of organic matter must be minute. The hydrogen was 0·17 per cent., but this is probably due to a small quantity of water combined or occluded, and the same remark may apply to the carbon, which may have existed as liquid carbon dioxide in the crystals. The "Blue John" after combustion was colourless.

It may be remarked that all these experiments were made on the mineral direct from the mine. Earlier experiments were made on "Blue John" prepared as ornaments, and at that time the authors were not aware that the handsomest specimens are filled with resinous matter in order to make them easier to handle and

to turn. Probably on this account other chemists have been mis-
led into the belief that the colouring material is organic, because
they have found organic matter in the samples which they ex-
amined, and supposed that it was of natural origin. It remains a
fact, however, that organic matter exists in "Blue John." This
organic matter is not affected by a temperature of 150°. When
a temperature of about 350° is reached, the "Blue John"
decrepitates and the colour disappears.

Gases from "Blue John."

On account of experiments, which will be described later, it was
supposed that the colour of "Blue John" might be due to the
action of radium, and many trials were made in this direction.
As is well known, glass is easily coloured by the rays from radium,
and a series of experiments was made by one of us.

While these experiments were proceeding, another method was
adopted for the same end. A fairly large quantity (about
50 grams) of "Blue John" direct from the mine, not impregnated
by any extraneous resinous material, was heated in a hard glass
tube, and the gases were pumped out. After the carbon dioxide,
hydrogen, and nitrogen had been removed, the remaining inert
gases were examined spectroscopically in a Plücker tube. Argon
was present, but helium was not. The deduction is that the gases
consisted only of those that occur naturally in rocks and minerals
which readily decrepitate.

Green Fluorspar "Green John."

This is similar to "Blue John," but decrepitates with greater
violence. Both varieties fluoresce on heating, the light from the
green kind being more vivid. Green fluorspar, called conveniently
"Green John," and so referred to hereafter, appears to be much
rarer than "Blue John," and it was only by the kindness of a
friend that a specimen of good quality was obtained. Others
taken from mines in Durham and Cornwall were evidently less
pure. As the quantity of good "Green John" available was some-
what small, our examination of it was necessarily limited, and the
gases which are given off on decrepitation were not analysed, the
quantity at our disposal being too small for any satisfactory
examination.

Systematic experiments by one of us (J. H. S.) were carried
out at the London Hospital on the action of radium and X-rays

on various samples of fluorspar. The notes made at the time are here recorded.

(A) *"Blue John": Experiments with Radium.*

(1) Two pieces of banded fluorspar ("Blue John") were exposed to radium, contact being made with a plate 2·5 cm. square containing 30 milligrams of radium salt under a varnish.

As a result of this exposure, both pieces of spar changed colour, the white parts becoming bright blue and the blue becoming darker. In ten days these changes were well marked.

(2) Pieces of "Blue John," "Green John," and white fluorspar were similarly exposed. In three days, a bright blue change was noticed in the white fluorspar, the "Green John" was slightly darker, and the "Blue John" much darker.

(3) Portions of "Blue John" were heated in glass tubes, and thereby decolorised. These decolorised specimens were then exposed to radium and to X-rays. The specimen exposed to radium for fourteen days became a light blue. The specimen exposed to X-rays for about twenty-four hours continuously became dark purple.

(4) A small portion of "Blue John," banded, was exposed for six hours to X-rays, and turned almost a dark violet colour.

The "Green John" exposed for fourteen days was distinctly darker in colour.

(B) *Experiments with X-Rays.*

(1) Half an hour's exposure at 7·5 cm. produced on:
    "Blue John," slight deepening.
    "Green John," no change.
    Fuorspar, change to violet shade.

The fluorspar, on being replaced in a drawer, returned to almost normal colour.

(2) Half an hour's exposure at 7·5 cm. produced on:
    "Blue John," slight deepening.
    "Green John," no change.
    Fluorspar, change to violet shade.

The fluorspar returned to almost normal colour.

(3) Forty-five minutes' exposure at 7·5 cm. produced on:
    "Blue John," more marked change.
    "Green John," no change.
    Fluorspar, more marked change.

The fluorspar almost recovered.
(4) Ten minutes' exposure at 7·5 cm. produced on:
    Fluorspar, light violet colour.
    No other change perceptible.
(5) Half an hour's exposure at 7·5 cm. produced on:
    "Green John," fluorescence.
    Fluorspar, change as before.

The "Green John," after being carried into a dark room, still fluoresced for about three or four minutes.
Fluorspar in a glass tube also fluoresced, but very slightly.
(6) Ten minutes' exposure at 7·5 cm. produced on:
    "Green John," slight fluorescence (both).

Material after resting for fourteen days:
    Fluorspar was pink with one mauve spot.
    "Blue John" was darker than when experiments started.
    "Green John" did not appear to have changed at all.

The fluorspar in glass was darker than at first.
None of the specimens exposed to X-rays made any change in photographic plates, even after prolonged exposure.
Even after colour changes had been produced by exposures to X-rays and radium, there was no evidence of radioactivity, as shown by exposure of a photographic plate.
From these experiments, it appears that there is no substantial difference between white fluorspar and "Blue John," except in respect of the small amount of organic matter which gives the colour of "Blue John."
The same seems to hold for "Green John" and for the amethystine varieties. It appears that the colouring matter is, after all, organic. The influence of X-rays and of radium on natural fluorspar appears similar to that on glass. The *causa causans* is unknown.
From a series of experiments which have now lasted more than two years, there is no reason to suppose that what in the earlier trials seemed to be a reasonable hypothesis, namely, that the colour of "Blue John" and other varieties of coloured fluorspar owes its origin to radioactive effect, has no foundation.

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LIX.—*Studies in Catalysis.   Part XI.   The Le Chatelier–Braun Principle from the Point of View of the Radiation Hypothesis.*

By WILLIAM CUDMORE McCULLAGH LEWIS.

THE object of this note is to point out that the quantum–radiation view of chemical reactivity is in agreement with the thermodynamic principle of Le Chatelier and Braun as applied to the effect of temperature on the equilibrium constant of a reversible reaction.
. Consider the reversible reaction :

$$\text{reactant} \rightleftharpoons \text{resultant}.$$
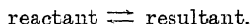
Let us suppose that the reaction from left to right is endothermic. Then, in accordance with the principle of mobile equilibrium, an increase in temperature will favour the resultants.

From the point of view of radiation, the fact that the above process is endothermic means that the critical increment of the resultant is less than that of the reactant. This follows from the quantum–heat expression :

heat evolved = critical increment of resultant *minus*

critical increment of reactant,

or heat evolved = $Nh(v_2 - v_1)$, where N is the Avogadro number and h is Planck's constant. In the case considered, it follows that the critical frequency v_2 of the resultant is less than the critical frequency v_1 of the reactant.

Let us consider the above equilibrium at two different temperatures, T_1 and T_2, where T_1 is less than T_2. For the short infrared region (which has already been shown to be of significance for reactions which proceed with measurable velocity at the ordinary temperature), as well as for the visible and ultra-violet regions, the radiation density corresponding with the frequency v_1 at T_1 is

$$\frac{8\pi h v_1^3 n^3}{c^3} \epsilon^{-h v_1 / k T_1},$$

and at T_2 the density is

$$\frac{8\pi h v_1^3 n^3}{c^3} e^{-h v_1 / k T_2},$$

where c is the velocity of light in a vacuum.

If T_1 and T_2 are not very far apart, and especially if the react-

ing system is gaseous, the refractive index term n will be practically the same at both temperatures.

The fractional increase in the radiation density, due to the rise in the temperature from T_1 to T_2 at the frequency ν_1, is given by

$$\frac{\frac{8\pi h\nu_1{}^3 n^3}{c^3}\left(e^{-h\nu_1/kT_2} - e^{-h\nu_1/kT_1}\right)}{\frac{8\pi h\nu_1{}^3 n^3}{c^3}e^{-h\nu_1/kT_1}}$$

which is equal to

$$e^{\frac{h\nu_1}{k}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)} - 1 \ \Big).$$

Similarly, for the fractional increase in the radiation density at the frequency ν_2 we obtain

$$\frac{h\nu_2}{k}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) - 1 \ \Big\rangle.$$

Since by hypothesis ν_1 is greater than ν_2, it follows from the above expressions that the fractional increase in the radiation density at the frequency ν_1 is greater than that at the frequency ν_2. Hence at the higher temperature the radiation density of the type absorbable by the reactant (ν_1) has increased *relatively* to that absorbable by the resultant (ν_2).

On the radiation hypothesis of chemical reactivity, it is assumed that the rate of decomposition is directly proportional to the radiation density. For both frequencies, the rise in temperature has caused an increase in the radiation density, but the increase is relatively greater for the higher frequency (ν_1) as compared with the lower frequency (ν_2). It follows, therefore, that at the higher temperature both the reactant and the resultant react or decompose more rapidly than they do at the lower temperature. This is in agreement with experiment. What is more important, however, is that the reactant decomposes at a relatively faster rate than the resultant, because the radiation density of the reactant is relatively increased with respect to that of the resultant. Hence as the temperature is raised, the existence of the resultant, in the above case, is favoured more than that of the reactant, and the equilibrium position shifts over towards the right. Had the reaction been exothermic, the relative positions of ν_1 and ν_2 would have been reversed, with the result that the equilibrium concentration of the reactant would have increased relatively to that of the resultant.

These conclusions are identical with those which are arrived at

on the basis of the principle of Le Chatelier and Braun.   The radiation hypothesis is therefore in complete agreement with the, thermodynamic generalisation; and, in fact, the conclusion regarding the direction of the change in the equilibrium position with temperature could be inferred on the radiation basis alone, without any direct appeal to thermodynamics.